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PARAMETRIC ANALYSIS OF CO_2 SEPARATION FROM NATURAL GAS BY ADSORPTION PROCESS

By

ABDURRAHMAN MUHAMMAD HAMID

A THESIS
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AS A REQUIREMENT FOR THE
DEGREE OF MASTER OF SCIENCE
CHEMICAL ENGINEERING

BANDAR SERI ISKANDAR
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Declaration

I hereby declare that the thesis is based on my original works except for quotations and citations which has been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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ABSTRACT

Many technologies are available today for CO_2 removal. Among the widely used technology are absorption, membrane technology, cryogenic, and adsorption. Each technology has its own advantages and disadvantages. In term of low capital and maintenance costs, high purity product, rapid shutdown-start-up, and lack of corrosions problems adsorption is a preferable choice.

Based on literature review, there are four adsorbents were identified to be the most suitable adsorbent for CO_2 removal from natural gas, which are 4A zeolite, 5A zeolite, 13X zeolite, and carbon molecular sieve (CMS). However, there were no rigorous adsorbent screening studies for CO_2/CH_4 separation. In this work, all the adsorbent were evaluated and compared for the separation of CO_2 from CH_4. The best adsorbent was selected based on selectivity (kinetic or equilibrium) and capacity. Information of adsorbent capacity and selectivity was obtained from adsorption isotherm and kinetic measurement. The measurements were performed by gravimetric method since it provides more accurate result compared to other methods.

The performance of the best adsorbent determined from the screening test was evaluated from parametric analysis study. The evaluation will led to the identification of the best operating conditions for the adsorption system. In this work, the effect of temperature, pressure, flow rate, and concentration on productivity, purity, and recovery were evaluated for bulk separation of CO_2 from CH_4.

The result from adsorption isotherm and kinetic measurement showed that CMS has the highest selectivity among other adsorbents. However, the binary adsorption isotherm shows that for bulk separation of CO_2, the adsorption capacity of CH_4 is reduced and the value approaches zero. Therefore, for bulk separation of CO_2, it is more important to select adsorbent that gives high CO_2 capacity rather than selectivity. In this study, 13X zeolite has the highest CO_2 capacity compare to other adsorbents.

The parametric study indicated that the regeneration of CO_2 was best performed by ambient temperature gas stripping only since high temperature will reduce productivity. Lower CO_2 composition in the feed mixture gives higher CH_4 recovery without significant effect on purity. The result show that 13X zeolite can be used to separate CO_2 from CH_4 even at 70% CO_2 composition with product purity better than 99% but with low recovery up to 83%. The variation of flow rate did not significantly affect purity and recovery. The adsorption system can still produce good CO_2 separation for the whole flow rate range used in this experiment. No significant result was observed in pressure variation study due to rapid breakthrough.

CONTENTS

LIST OF FIGURES

APPENDIX D

LIST OF TABLES

ABBREVIATIONS

BET	Brunauer Emmet Teller
CNG	Compression Natural Gas
CMS	Carbon Molecular Sieve
DEA	Di Ethanol Amine
EOS	Equation of State
FID	Flame Ionization Detector
GACU	Gas Adsorption Column Unit
GC	Gas Chromatography
IAST	Ideal Adsorbed Solution Theory
ID	Inside Diameter
LPG	Liquefied Petroleum Gas
LNG	Liquefied Natural Gas
MEA	Mono Ethanol Amine
MMSCFD	Milion Square Feet per Day
MSB	Magnetic Suspension Balances
MTZ	Mass Transfer Zone
MP	Measuring Point
NGL	Natural Gas Liquid
NRU	Nitrogen Rejection Unit
OD	Outside Diameter
PSA	Pressure Swing Adsorption
SS	Stainless Steel
TCD	Thermal Conductivity Detector
TSA	Thermal Swing Adsorption
VST	Vacancy Solution Theory
ZP	Zero Point

NOMENCLATURE

Symbols

A	Surface area	m^2
b	Empirical fitted constant.	
Cp	Heat capacity	lb-mol/ lb °F
C	Concentration	Molar
D	Diffusivity	cm^2/s
D_m	Bulk diffusion	cm^2/s
D_k	Knudson diffusion	cm^2/s
D_p	Poisuille diffusivity	cm^2/s
D_∞	Diffusivity pre-exponential factor	cm^2/s
F_A	Weight of MSB system	N
F_B	Bouyancy forces	N
F_{TOT}	Total forces from MSB	N
g	Gravity constant	m/s^2
K	Henry's constant	mmol/gr.bar
M	Molecular weight	g/mol
m_{SC}	Mass of sample container	g
m_{SC+S}	Mass of sample container + sample	g
$m_{SC+S+\Delta m}$	Mass of sample container + sample + adsorbate	g
m_S	Mass of sample	g
m_A	Mass of adsorbate	mg
m_t	Mass of adsorbate as function of time	mg
$m_\sim$	Mass of adsorbate at equilibrium	mg
m_l	monolayer load	mg
Δm, m_{BAL}	Mass balances reading	g
m_{gas}	Mass of gas	mg
n	Empirical fitted constant	
q	Adsorbent capacity	mmol.g
q_s	Maximum capacity	mmol/g

Table 1.1 Raw natural gas compositions (NGA, 2004).

Typical Composition of Natural Gas		
Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen Sulphide	H_2S	0-5%
Rare gases	Ar, He, Ne, Xe	Trace
Metals	Ni and Hg	Trace

The natural gas goes through a series of chemical processes to remove the impurities and to increase its heating value. The gas is then transferred to a pipeline for distribution. A typical pipeline natural gas specification is given in Table 1.2 and a typical pipeline natural gas combustion properties is given in Table 1.3.

Table 1.2 Pipeline natural gas specifications (Union Gas, 2006).

Component	Typical Analysis (Mole %)	Range (Mole %)
Methane	94.9	87.0 - 96.0
Ethane	2.5	1.8 - 5.1
Propane	0.2	0.1 - 1.5
Iso - Butane	0.3	0.01 - 0.3
Normal - Butane	0.03	0.01 - 0.3
Iso - Pentane	0.01	trace - 0.14
Normal - Pentane	0.01	trace - 0.04
Hexanes plus	0.01	trace - 0.06
Nitrogen	1.6	1.3 - 5.6
Carbon Dioxide	0.7	0.1 - 1.0
Oxygen	0.02	0.01 - 0.1
Sulphur	-	<5.5 mg/m^3
Water	16-32 mg/m^3	<80 mg/m^3
Hydrogen	Trace	Trace - 0.02

Table 1.3 Pipeline natural gas combustion properties (Union Gas, 2006).

Combustion Properties	Value
Ignition Point	593°C
Gross Heating Value (dry basis)	36-40.2 Mj/m3
Flammability Limit	4-16% volume in air
Theoretical Flame Temperature	1960°C
Maximum Flame Velocity	0.3 m/s
Relative Density	0.585

The natural gas composition may vary widely based on geographical location. In Xinjiang, China, the reservoir has only trace amount of CO_2 and H_2S and the methane content is about 70% (Berger et al, 2003). Usually, natural gas contents about 0-8% CO_2. However, there are some reservoirs that content CO_2 higher than 8%. A more severe case occurs in Natuna field, Indonesia with an average gas composition consisting of 71% CO_2, 28% methane and heavier gases, and about 0.5% nitrogen. A lot of effort needs to be done in order to reduce the CO_2 content to meet pipeline quality (<2%) and LNG (<200 ppm) specification (APS, 1999).

1.2 CO_2 Separation Technology

In natural gas, CO_2 occurrence has led to many disadvantages. CO_2 is a very corrosive gas, especially in the presence of water. The heating value of the natural gas is reduced if high CO_2 content is present (CO_2 has lower heating value compared to natural gas), which subsequently reduces the price natural gas per unit volume. In LNG processes, the natural gas is cooled down to -160°C. At that temperature, carbon dioxide will solidify. When this happens, it may block the pipe and causes transportation problem. In steam reforming process, the presence of CO_2 will shift equilibrium to the reactant side and hence reduce maximum conversion of the reaction.

Several methods are available for the separation of CO_2 from natural gas such as absorption, membrane separation, low temperature distillation (cryogenic) and

adsorption. Each method has its own advantages and disadvantages which will be discussed in the next section.

1.2.1 Absorption

Absorption is the most widely used CO_2 separation technology. Most of the CO_2 separation processes utilize this technology. Based on the absorbent material used, absorption can be classified into two types physical or chemical absorption. Physical absorption is based on the solubility of CO_2 to specific solvent, while chemical absorption is based on the chemical reaction between CO_2 and the absorbent.

Between the two types, chemical absorption is more frequently used. Among the widely used solvents are Mono Ethanol Amine (MEA), Di Ethanol Amine (DEA), and Benfield (K_2CO_3). Those solvents will react with CO_2 to become intermediate component. For example, in the case where the Benfield solution is utilized, the Benfield solution (K_2CO_3) will react with CO_2 to form potassium bicarbonate ($KHCO_3$) according to the reaction below:

$$K_2CO_{3\,(aq)} + CO_{2(g)} + H_2O_{\,(l)} \Leftrightarrow 2KHCO_{3(aq)}$$

This absorption process is usually held at high pressure and low temperature to obtain good absorption of the solvent because the process is exothermal. On the other hand, the regeneration of CO_2 from the solvent is usually held at low pressure and high temperature.

In physical absorption, CO_2 is physically absorbed in a solvent according to Henry's law. Based on Henry's law, the solubility is increased at high pressure and low temperature. The advantage of this method is it only requires a small amount energy for regeneration. However, for better absorption, CO_2 partial pressure must be kept high. Typical solvents for physical absorption are Selexol (dimethylether of polyethylene glycol) and Rectisol (cold methanol) (Arnold, 1999).

The major disadvantage of absorption process is the corrosive properties of the absorbent. To minimise this problem, anti corrosion agent is constantly injected into the system. Anti foaming agent is injected to reduce the surface tension of the

absorbent and to ensure better contact between the absorbent and CO_2. The disposal of absorbent creates another problem. Since the used absorbent may harm the environment, therefore additional treatment needs to be done prior to disposal (Perry and Green, 1997).

1.2.2 Membrane Separation

Membranes consist of thin barriers that selectively permeate certain gases. Generally, membranes are made from polymeric materials even though organic membrane is also used in a lesser extent. Membranes usually take the form as hollow fibres arranged in a tube-and-shell configuration or as flat sheets. They are typically packaged as spiral-wound modules. The membrane process has been widely used for hydrogen recovery from purge gases in ammonia synthesis, refinery and natural gas dehydration, sour gas removal from natural gas, and nitrogen production from air. The schematic diagram of membrane process is shown in Figure 1.1 below.

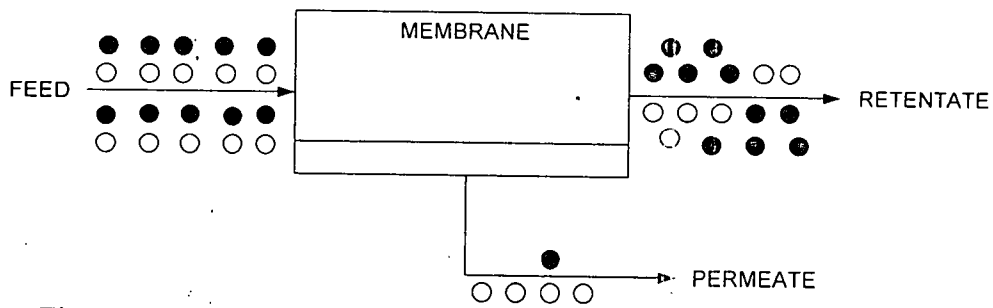


Figure 1.1 Schematic diagram of membrane process.

There are two mechanisms that govern membrane separation. The first mechanism is a solution diffusion mechanism. In this mechanism, the permeate dissolves in the membrane material and diffuses through the membrane due to concentration gradient. Permeate is separated from retentate based on solubility and diffusivity difference of the component in the membrane. Another mechanism is the pore flow model. In this mechanism, permeates are transported by pressure-driven convective flow through tiny pores. Separation happens due to the size differences among the components. Only component which has smaller size than the pore can pass through the membrane (Baker, 2004).

There are many advantages of using a membrane. The membrane system are compact and lightweight and can be designed for either horizontal or vertical position. Membrane system does not require any separating agent, therefore, no regeneration is required. Another advantage of the membrane system is that it only requires low maintenance.

In spite of its advantages, there are several issues regarding this technology especially when handling CO_2 gas. The CO_2 occurrence may cause swelling on the membrane pore and the membrane will no longer act selectively to separate the mixture. This normally happens for polymer based membrane. In comparison to other methods, the membrane system cannot withstand too high pressure and temperature and can produce only lower flux compare to other methods (Baker, 2004).

1.2.3 Cryogenic Technology

Cryogenic separation is a process commonly used to liquefy and purify gas at very low temperature (below 0°C). This type of separation sometime is also called low temperature distillation. The main principle of this separation is based on boiling point differences of each component. Nevertheless, the separation into pure components is influenced by the composition of the gas being cooled (Mc Kee, 2002).

Cryogenic method generally has good economies of scale for bulk separation (>10% of CO_2). This separation requires no additional water and chemicals, thus no further separation is required. For natural gas sweetening, the liquid CO_2 produced is ready for easy transportation and does not require compression (Mc Kee, 2002).

However, the main disadvantage of cryogenic separation is its high energy consumption mainly required for the refrigerant compressor, therefore this process is not cost effective for purification purposes. This process requires the removal of water and other condensable gas, have to be removed before the gas stream is cooled to avoid freezing and eventual blockage of process equipment. Additional separation is also required in the sweetening stage since about 10% of hydrocarbon components are also present together with CO_2. These two additional separation steps incurred

extra cost, which contributed to the high cost of instalating the system (Mc Kee, 2002).

1.2.4 Adsorption

Generally, adsorption separation is based on selectivity difference of a gas mixture on a microporous surface. When a gaseous mixture is exposed to an adsorbent within sufficient time, there will be an equilibrium between the gas phase and the adsorbent phase. The attractive forces between the adsorbent and the gas phase are mainly controlled by van der Waals force. However, in several cases adsorption separation can be based on adsorption rate differences or molecular sieving effect. The saturated adsorbent can be regenerated in desorption step. The desorption step can be accomplished by reducing the system pressure or increasing the temperature. By manipulating the system pressure or temperature, the adsorption and desorption steps can be done continuously in a cycle.

Based on the regeneration method, the adsorption system can be differentiated as pressure swing adsorption (PSA) and thermal swing adsorption (TSA) (Burchell et al., 1997). The choice of adsorption methods depends on economic factor as well as technical consideration. Major advantages in PSA system are low capital and maintenance costs, high purity product, rapid shutdown and start-up characteristics, lack of corrosion problems, absence of heat requirement and pipe insulation and comparative straight forward operation. In contrast, PSA has disadvantages due to it's high pressure and vacuum pressure requirement, which contribute to high operating cost. On the other hand, thermal swing adsorption TSA is very reliable to remove minor component. The main obstacle in thermal swing adsorption is the adsorption cycle time limitation due to the time required to cool down the bed. Other obstacles are the high energy requirements and large heat loss (Burchell et al., 1997).

Adsorption process is scarcely applied in bulk separation of CO_2 from CH_4. However, kinetics-based adsorption has been implemented for recovery of methane from landfill gas in USA. These gases contain mainly methane (50-65 %), carbon dioxide (35-50%), a small amount of nitrogen and a trace amount of sulphur

compounds. The adsorbent used in this process is carbon molecular sieve. This process can recover more than 90 % methane with 87-89% purity (Kapoor and Yang, 1989).

Another successful application for bulk separation of CO_2 from CH_4 is performed by using Engelhard molecular gate, a commercial brand name adsorbent developed by Engelhard Corporation. The first application of molecular gate CO_2 removal system is at the Tidelands Oil Production Company operated facility in Long Beach, California. The feed source for the unit is hydrocarbon rich associated gas from enhanced oil recovery section. The feed is typically operated at 30-40% of CO_2 and the adsorbent is able to reduce the CO_2 level to less than 2% (Ulrich, 2005).

1.3 Adsorbent for Gas Separation

Almost every separation process requires mass separating agent. Adsorbent is the mass separating agent for adsorption separation and is specific for each adsorption mechanism. There are three distinguished adsorption mechanism namely steric, kinetic and equilibrium mechanism. Most of the separation processes are based upon equilibrium mechanism. The separation is accomplished by the adsorption equilibrium capacity difference of the adsorbent among the adsorbate. In steric mechanism, separation is performed due to the molecular sieving property of the adsorbent. In this mechanism, big molecules are excluded and only small and properly shaped molecules can diffuse on the adsorbent. While in kinetic mechanism, the separation is determined by diffusion rate differences among the adsorbate molecules (Yang, 2003).

Due to its uniform pore size, zeolite and molecular sieves are suitable for steric mechanism adsorption. Only few adsorption processes are based on this mechanism. Two main areas of applications are gas dehydration using 3A zeolite and the separation of n-parafin from iso-parafin and cyclic hydrocarbon by 5A zeolite.

The starting point for adsorbent selection in equilibrium separation is to examine the fundamental properties of the targeted molecules such as polarizability, magnetic susceptibility, permanent dipole moment and quadrapole moment. Activated carbon

with a high surface area is suitable if the targeted molecule have high polarizability and magnetic susceptibility but no polarity. If the targeted molecules have a high dipole moment, adsorbents with high polarity such as activated alumina, silica gel, and zeolites are the best option. Zeolites that have high electric field gradient are suitable to adsorb molecules with high quadrapole moment.

For kinetic separation, the adsorbent pore size needs to be tailored exactly to a certain value between the kinetic diameters of two adsorbates that are to be separated. Many microporous molecular sieves have been manufactured for this purpose. Air separation on carbon molecular sieves is a good example for kinetic separation. In this process, oxygen diffuses 30 times faster than nitrogen even though the adsorption capacities are approximately the same.

Adsorbent selection is normally based on the adsorbent selectivity and capacity. The selectivity of the adsorbent depends on adsorption mechanism. Equilibrium selectivity is a function of Henry's constant ratio of the adsorbate, whereby the kinetic selectivity depends on both Henry's constant ratio and diffusivity ratio of the adsorbate. The adsorbent capacity can be observed from the adsorption isotherm curve. Detailed explanation of the adsorbent selection is given in chapter 3.

The commercial use of adsorption has been dominated by mainly four types of adsorbent: activated carbon, zeolites, silica gel and activated alumina. Zeolite and carbon molecular sieve are generally utilized for CO_2/CH_4 separation. The characteristic of these adsorbents will be discussed in the next section.

1.3.1 Activated carbon

Activated carbon generally is made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature (700-1100°C). The structure of activated carbon consists of mycrocrystalite graphic stacked together in random distribution. This random distribution causes the pore size of activated carbon to be non uniform.

The activated carbon surface is basically non polar although a slight polarity may exist due to the surface oxidation. Therefore, activated carbon tend to be organophylic

or hydrophobic. Based on this behavior, activated carbon is widely used for decolorizing sugar, water purification, solvent recovery, and for the adsorption of gasoline vapors (Ruthven, 1988).

1.3.2 Carbon Molecular Sieve

Activated carbon is not able to do selective separation based on molecule size differences. A special treatment is required to produce activated carbon with uniform pore size distribution and therefore it behaves as molecular sieves. Generally, carbon molecular sieve are prepared from hard coal by controlled oxidation and subsequent thermal treatment. The pore structure can be modified by controlled cracking of hydrocarbons within the micropore system and partial gasification under carefully regulated conditions (Yang, 2003).

The micropore sizes distribution of carbon molecular sieves are much narrower than activated carbon, therefore the adsorption capacity is lower. It is relatively easy to modify the effective pore size of carbon molecular sieves by careful controls of concentration, time, and temperatures. However, it is difficult to achieve reproducibly between different batches. Well-prepared carbon molecular sieves may have remarkably high kinetic selectivity (Ruthven, 1988).

1.3.3 Zeolite

Zeolite is porous crystalline aluminosilicates of alkali or alkali earth such as sodium, potassium, and calcium. The chemical composition of zeolite is represented as

$$M_{x/n}((AlO_2)_x(SiO_2)_y).{}_zH_2O$$

where x and y are integers with y/x are greater than 1, n is the valence of cation M, and z is the number of water molecules in each unit cell. The primary structure of zeolite consists of tetrahedral SiO_4 and AlO_4 joined through shared oxygen atoms. The shared oxygen bonding forms an open crystal lattice containing pores of molecular dimensions into which guess molecule can penetrate. These units are

further assembled into secondary polyhedral building such as hexagonal, cube, octahedral and truncated octahedral. The final structures consist of the secondary unit in three-dimensional crystalline framework. The secondary unit and three-dimensional crystalline framework are shown in Figure 1.2. The pore size of zeolite is uniform (without pore size distributions). These features distinguish zeolite from the traditional microporous adsorbent (Ruthven, 1988).

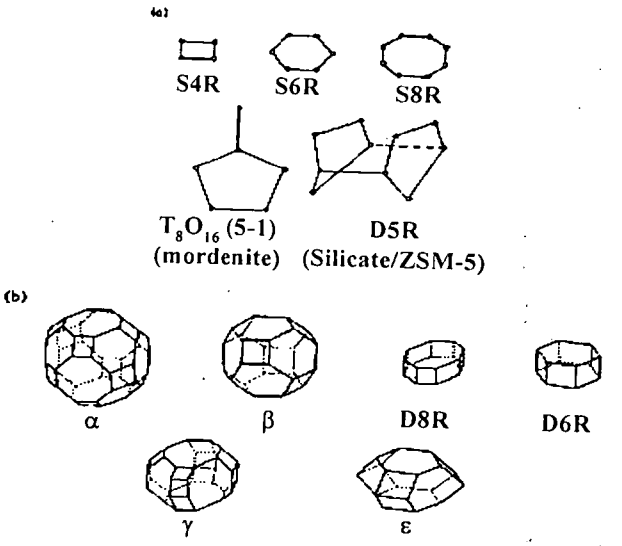


Figure 1.2 (a) Secondary building unit and (b) three dimensional crystalline network (Ruthven, 1988).

The aluminum atom contains one negative charge that must be balanced by an exchangeable cation. This exchangeable cation plays a very important role in determining the adsorption properties. Changing the exchangeable action can modify the adsorption properties (Ruthven, 1988).

The kinetic selectivity and the molecular sieve properties are determined mainly by the free diameter of the window in intercrystalline channel structure. For instance, in sodalite type zeolite the channel free diameter is only 2.8 Å. Therefore, only small polar molecules such as H_2O and NH_3 can penetrate this pore. In the small pore zeolite such as zeolite A, chabasite, and eronite the limiting diameter is 4.2 Å while in higher pore zeolite such as zeolite X, zeolite Y and mordenite the limiting diameters are 7-7.4 Å (Ruthven, 1988).

In commercial adsorption separation, there are two types of zeolite that are generally used, zeolite A and zeolite X. The structure of zeolite A is shown in Figure 1.3 below.

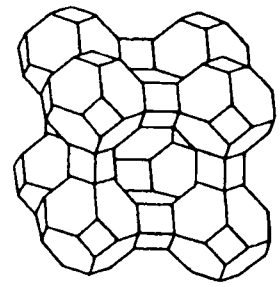


Figure 1.3 Zeolite A structure (Ruthven, 1988).

Each pseudo cell consists of eight β cages at the corners of the cube and is connected through a four-membered oxygen ring. Each pseudo cell consists of 24 tethedral (AlO_2 and SiO_2) units. Since the Si/Al ratio in zeolite A is always close to one, therefore there are 12 univalent exchangeable cations per cell. The zeolite type depends on the exchangeable cation. For 4A and 5A zeolites, the exchangeable cations are sodium and calcium/magnesium respectively. Bigger cation size will partially obstruct the pore size. The effective pore size for 4A zeolite is 3.8 Å while the effective pore size for 5A is 4.3 Å (Ruthven, 1988).

The framework structure of zeolite X is shown in Figure 1.4 below. The framework consists of 192 AlO_2 and SiO_2 tetrahedral units. The effective pore size of this type of zeolite is ~7.4 Å with Si/Al ratio 1-1.5.

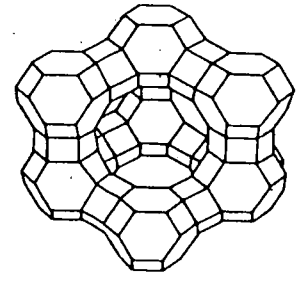


Figure 1.4 Zeolite X structure (Ruthven, 1988).

The exchangeable cation in zeolite X can vary from 10-12 cation with Na^+ as the major exchangeable cation. The cation distribution depends on the number of the cations and trace moisture present. There is an evident that the cation distribution may change when the sieve is loaded with the adsorbent. The variation in adsorptive

properties may occur due to redistribution of the cation. Nevertheless, the relationship between adsorption properties and cationic distribution is not fully understood (Ruthven, 1988).

1.4 Adsorption Isotherm

In the adsorption process, the adsorbent and the surrounding fluid reach equilibrium after sufficient contact time. The adsorbed amount can be determined from the adsorption isotherm as shown in Figure 1.5 below. Adsorption isotherm is a correlation between the adsorbed amount (q) and the concentration for liquid system (C) or pressure (P) for gas system, at constant temperature.

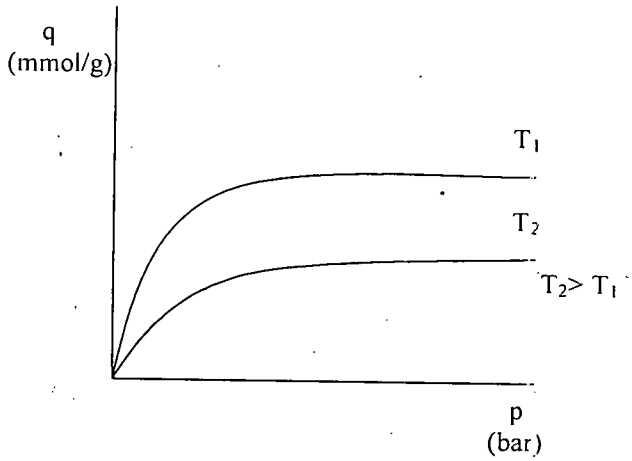


Figure 1.5 Adsorption isotherm curve.

Adsorption performance can be predicted from the adsorption isotherm. Several important informations required for process design such as maximum capacity, equilibrium selectivity and breakthrough time, can be extracted from adsorption isotherm. The adsorbent capacity increases as pressure increases until a certain value called the maximum capacity, where the pressure increment no longer affects the capacity. The maximum capacity provides information of optimum pressure required for single component separation. Adsorption isotherm can be used to predict breakthrough time. The breakthrough time can be calculated by dividing the molar inlet flow rate of the component to its capacity. For multicomponent separation,

adsorbent selectivity is very important. The detail calculation of adsorbent selectivity from the adsorption isotherm will be discussed in chapter 3.

1.5 Adsorption Isotherm Measurement

Several methods exist to measure adsorption equilibrium. Among the most widely used methods are gravimetric, volumetric, and chromatographic. In gravimetric method, the total adsorbed amount can be easily predicted by a simple flow apparatus, in which the sample is sealed of, disconnected and weighted after the equilibrium is reached. The development of Magnetic Suspension Balances (MSB) gravimetric method enabled the adsorption measurement at high temperature and high pressure. Detail technique of MSB gravimetric method will be given in chapter 4.

In volumetric method, the amount of gas before and after the adsorption take places is calculated. The total amount can be predicted by pressure and volume relationship. The volumetric adsorption isotherm apparatus is shown in Figure 1.6 below. The apparatus consist of two compartments, which are the reservoir as indicated by the striped area, and the sample container, including the sample itself. Volume of both compartments can be predicted accurately by helium displacement. The total adsorbed amount can be calculated from the pressure transducer reading (Yang, 1987).

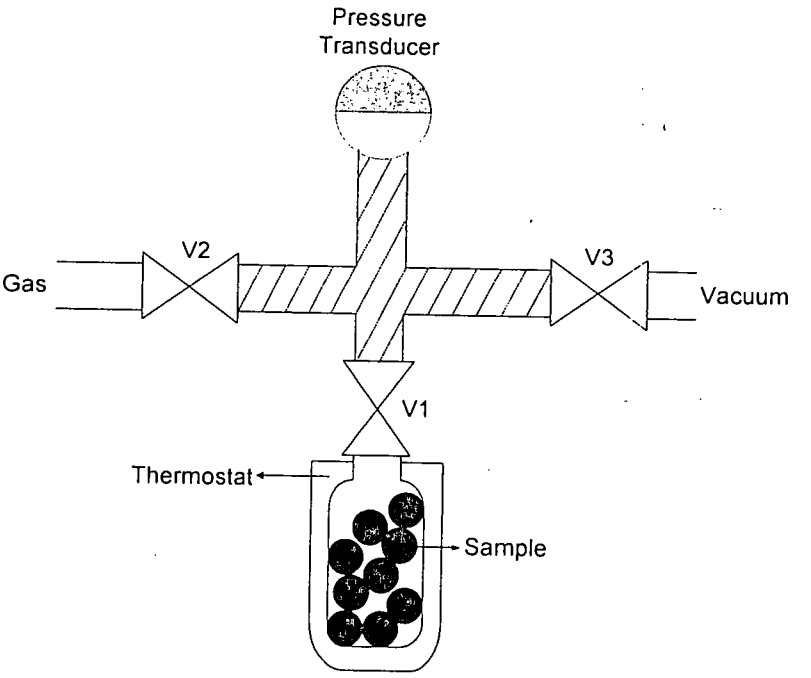


Figure 1.6 A schematic diagram of volumetric adsorption isotherm apparatus.

The chromatographic method has been used for adsorption isotherm measurements since decades. In this technique, a small dose of the component is injected into a constant flow of inert gas, such as helium. The stream is introduced to the adsorbent bed and the thermal conductivity of the gas is measured before and after the bed. The retention time can be calculated by analysing the conductivity differences between the pure inert gas and the introduced feed. A simplified chromatography adsorption isotherm measurement apparatus is shown in Figure 1.7 below. From the retention time, the retention volume can be calculated. The retention volume, caused by the exchange of gases between the gas and adsorbed phase, then yields equilibrium relationship between the gas and the adsorbed phase. Detail measurement technique of chromatography and volumetric can be obtained in adsorption text books such as Yang (1987), Ruthven (1988), and Ruthven et al. (1994).

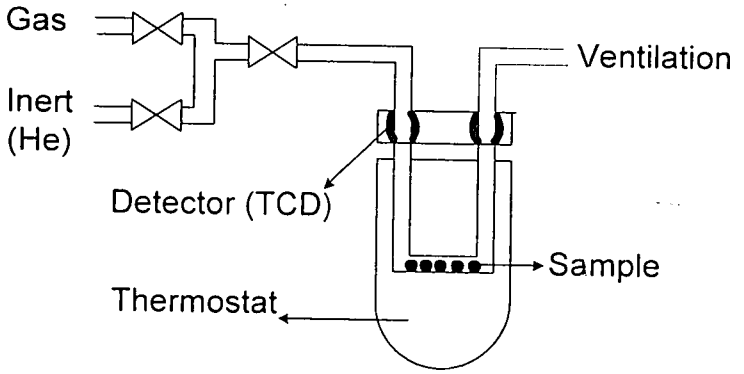


Figure 1.7 A schematic diagram of chromatograpic adsorption isotherm apparatus.

Each technique has specific advantages and disadvantages, as shown in Table 1.4. It is obvious that the gravimetric technique, especially after the development of Magnetic Suspension Balances (MSB), provides more accurate result.

Table 1.4 Adsorption isotherm measurement comparisons.

NO	Method	Advantages	Disadvantages
1	Volumetric	- Simple set up and operation - Only require P and T measurement - Direct T-measurement of sample	- Indirect measurement - Error accumulation - Requires relative high sample amount - Wall adsorption on instrument - Requires dead volume measurement - Sample activation cannot be checked
2	Chromatographic	- Simple and robust set up - No vacuum required - Only requre small sample amount	- Indirect Measurement - Error accumulation - Requires calibration measurement - Sample volume cannot be considered in material balance - Low accuracy
3	Gravimetric	- Direct measurement - High accuracy and no error accumulation - Only require small sample amount - Sample activation can be measured	- Complexity of the apparatus - Complexity of the experimental procedure

1.6 Dynamic Adsorption

The information determined from adsorption isotherm measurement can only be applied in ideal system in which the adsorption selectivity is based on the difference in equilibrium. In actual condition, dispersive effect such as axial mixing or finite resistance to mass transfer is substantial. For instance, in bulk separation velocity varies through the bed because significant amount of the feed stream is adsorbed.

Furthermore, the equilibrium theory cannot be applied in kinetic base system. Due to the limitation of information from the adsorption isotherm, it is crucial to investigate the dynamic adsorption in order to predict the actual behavior of the system.

Many models have been developed and tested with dynamic adsorption experiment. Generally, the developed models depend on the fluid flow pattern, constant or variable fluid velocity, the form of the equilibrium relationship, the form of the kinetic rate, and the inclusion of the heat effect. Those models can accurately predict the effect of several variables to the adsorption performance. Generally, the adsorption performance is described in term of product purity and recovery.

Many variables may affect the product purity and recovery such as temperature, pressure, concentration, flow rate, purge gas flow rate, purge gas quantity, reflux ratio, and purge to adsorption pressure ratio. Among those variable effect, the effect of temperature, pressure, concentration, and flow rate are the major contributors since those variables usually govern the economic value of the adsorption separation. For detail explanation of the effect of those variables to process performance please refer to chapter 2.

1.7 Problem Statement

The improvement of molecular sieve and synthetic zeolite production technology leads to the development of reliable adsorption separation system for the removal of carbon dioxide from methane. Some related studies use 4A zeolite, 5A zeolite, 13X zeolite, and carbon molecular sieve as the adsorbent (Triebe et al., 1995; Hernandez et al., 1997; Ding et al., 1999; Kovach, 1998; Paksereshy et al., 2002; Harlick et al., 2004; and Hyung-wong et al., 2004). They claimed that those adsorbents have good potential to be used for separation of CO_2 from natural gas. In order to select the best adsorbent among those adsorbents, a screening study should be done first. Generally, the screening criteria are based on equilibrium or kinetic selectivity and adsorbent capacity. The equilibrium selectivity can be determined from Henry's constant ratio while kinetic selectivity can be obtained from Henry's constant ratio and diffusivity

ratio. These parameters can be obtained from adsorption isotherm and kinetic measurements.

The adsorption isotherm and kinetic of CO_2 and CH_4 on the adsorbents can be measured using various different techniques. Conventional techniques for the adsorption isotherm and kinetic measurements are gravimetric, volumetric, and chromatographic methods. The accuracy of the measurement can vary depending on the measurement technique used. In some cases, the adsorption isotherm and kinetic measurement obtained by the same method but by different researchers show significant differences due to the different operating conditions used. Therefore, to compare the performance of the adsorbent for separation of CO_2 from natural gas, the adsorption isotherm measurement has to be done by the same technique and operating conditions. Unfortunately, there are no publication that shows a comparison of the performance of the adsorption by using the same technique and operating conditions. Furthermore, only Kapoor and Yang, (1989) have measured the most important adsorption isotherm parameters, which are Henry's constant, maximum capacity, and diffusivity for CO_2 and CH_4 separation but their studies were limited to carbon molecular sieve.

In comparison to the conventional adsorption isotherm measurement method, the gravimetric magnetic suspension balances provide more accurate result, despite its complexity. The system may detect the adsorbate weight change down to 1μg. It is very difficult to achieve this accuracy by other adsorption isotherm measurement technique. Nevertheless, there are very limited publication, if ever exist, of the adsorption isotherm measurement of CO_2/CH_4 on 4A zeolite, 5A zeolite, 13X zeolite, and carbon molecular sieve by using magnetic suspension balances.

Once the best adsorbent is obtained, the adsorption system in dynamic study need to be evaluated. The evaluation will lead to the determination of the best operating condition for the adsorption system. The adsorption performance is evaluated in term of productivity, purity, and recovery. The performance of the adsorption system can be evaluated from parametric analysis study. The most important parameters to be studied are temperature, pressure, flow rate, and concentration. Unfortunately, the parametric analysis study for CO_2/CH_4 separation is very rare. Only Kapoor and

Yang, (1989) have performed parametric analysis study for CO_2/CH_4 separation. However, their study is only limited to carbon molecular sieve. For that reason, it is important to study a detail parametric analysis of adsorption system in order to understand the effect of pressure, cycle time, concentration, and temperature to purity and recovery.

1.8 Objective of Study

The objectives of the research are:

1. To undertake screening studies of some potential adsorbents for CO_2 removal from natural gas.
2. To perform parametric analysis on selected adsorbent in order to study the effect of operating parameters to the performance of the process.

1.9 Scope of Study

Since natural gas contains approximately 95% methane and little amount of ethane, propane, butane, and other impurities, therefore, in this study, methane is selected as the only component to represent natural gas.

There are many types of adsorbents that are commercially available. However, there are only few adsorbents that are claimed as capable to effectively separate CO_2 from natural gas. These adsorbents are 4A zeolite, 5A zeolite, 13X zeolite and carbon molecular sieve. Only these adsorbents will be used in this study.

Generally, the best adsorbent is selected based on selectivity and capacity. In order to determine selectivity and capacity, Henry's constant and diffusivity information are required. These data can be obtained from adsorption isotherm and kinetic measurements. Even though there are many methods available for adsorption isotherm measurement, gravimetric method is used in this work due to its better accuracy.

Many parameters could be used in the parametric analysis. Only bulk separation is considered in this work (more than 10% of CO_2). In this study only the effect of

pressure, concentration, flow rate and regeneration temperature are selected due to their vital contribution for separation performance. In order to study the effect of the selected operating condition the other variable should be set to a certain fix value. The concentration and flow rate effect study is performed at ambient temperature and pressure. In adsorption study, the separation performance is evaluated based on purity and recovery of the product, whereby for regeneration temperature effect study, productivity is selected to determine the separation performance. The concentration and flow rate effect study is performed at ambient temperature and pressure.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Adsorption process has become increasingly popular as an alternative solution for natural gas separation from CO_2. Since natural gas consists of many components, as shown in Table 1.1, the adsorption process become more complicated. In order to simplify the study and due to its abundance in natural gas, approximately 95%, CH_4 has been chosen by many researchers to represent natural gas (Rolniak and Kobayashi, 1980; Hernandez et al., 1997; Nodzenki, 1998; Pakseresh et al., 2002).

An optimum design of adsorption process is a complex task including selection of the best adsorbent type and operating condition. In this chapter, potential adsorbents for CO_2/CH_4 separation that have been used by other researchers are reviewed. The effect of operating conditions to the adsorption performance is also be reviewed in this chapter.

Selection of suitable adsorbent for CO_2/CH_4 separation is very important since the primary requirements for an economic separation process is an adsorbent with high capacity and selectivity (Ruthven, 1988). Most researchers are concern in exploring the adsorption properties parameters of each gas on certain adsorbent. Among the important parameters are Henry's law constant, maximum capacity and diffusivity (Yang, 2002). These parameters are required to determine the selectivity of the adsorbent to be applied for CO_2/CH_4 separation. In this chapter, the adsorption characteristic of potential adsorbents for CO_2/CH_4 separation is reviewed. The reviews are not only focused on the adsorption of CO_2/CH_4 mixture but also the adsorption of CO_2 or CH_4 individually even for different separation purposes, such as the adsorption of CO_2 for air purification. The adsorption studies of other gasses will not be discussed here.

Many combinations of the operating conditions can be utilized to obtain good separation performance. The performance of a system normally can be analyzed

based on purity, recovery, productivity, breakthrough time and depletion time. However, most of the researchers determine the performance of a system based on purity and recovery. Since published literatures on parametric analysis of CO_2/CH_4 adsorption system are very scarce, therefore the parametric analysis studies for other adsorption systems are discussed here. Even though certain parameters are affected in other systems, but it is not necessarily applicable to CO_2/CH_4 system. However, the review will still provide sufficient information to identify the operating condition that required optimization. The review is mainly focused on the effect of operating conditions to the process performance.

2.2 Carbon Dioxide Adsorption

The adsorption of CO_2 on activated carbon was studied by Triebe and Tezel (1995) by chromatographic method. The adsorption isotherm in their study was based on Henry's model where the pressure increased linearly with the capacity. The main objective of their study was to remove CO_2 from air. The result of their study is shown in Table 2.1. It is observed that the Henry's constant obtained in their study is smaller than the adsorption of CO_2 on other adsorbents that used the same method. However, the adsorbent capacity was not reported in their literature.

Sriwardane et al. (1999) investigated CO_2 adsorption from flue gas. In their study, the adsorption isotherms of CO_2 on 13X zeolite and activated carbon were measured by volumetric method. The results of their experiments are shown in Table 2.1. Even though activated carbon has higher maximum capacity than 13X zeolite, but the capacity of 13X zeolite is higher at pressure less than 250 psi.

Beside the adsorption isotherm measurements, Sriwardane et al. (1999) also measured the desorption isotherm. The capacity of the adsorbents was also calculated from higher to lower pressure. The pressure reduction forced some of the gases to be desorbed. It is observed that the desorption isotherm curve of 13X zeolite overlappes with its adsorption isotherm curve. This situation indicates that the adsorption is reversible. On the other hand, the CO_2 desorption isotherm curve for activated carbon does not overlap with its adsorption isotherm curve, thus indicating that the CO_2 is

still trapped on the adsorbent even at ambient pressure. However, the activated carbon can still be regenerated by vacuuming the sample to $5x10^{-5}$ Torr.

Ding et al. (1999) conducted an experiment to study the equilibrium and kinetics of CO_2 adsorption on hydrotalcite at high temperature. The experiment gave more emphasis on CO_2 adsorption for steam reforming process. The measurement condition was chosen at the steam reforming temperature, at 753 K, and the measurement was performed by using dynamic column breakthrough method. The adsorption capacity was calculated from the inlet flow rate and break through time. The Langmuir model was used to describe the adsorption isotherm. Even though this technique is rarely used in adsorption isotherm measurements but it was adequate for their purpose (Ruthven, 1988; Staudt and Keller, 2002). The results indicate that hydrotalcite is suitable adsorbent for steam reforming process. The adsorbent maximum capacity at 753 K is 0.58 mol/kg. Nevertheless, in natural gas purification, the adsorption is only performed at ambient temperature since at high temperature the adsorption capacity can be reduced (Ruthven, 1988; Ruthven et al. 1994; Yang, 1987). A major disadvantage of hydrotalcite adsorbent is due to its strong adsorption, which requires tremendously high energy to regenerate the column.

Harlick et al. (2004) performed adsorbent screening study to select the best adsorbent for carbon dioxide removal from nitrogen using zeolite based adsorbents. The adsorbents that they studied were 5A, 13X, NaY, NaY-10, H-Y-5, H-Y-30, H-Y-80, HiSiv 1000, H-ZSM-5-80, H-ZSM-5-280, and HiSiv 3000. In their study, several adsorption parameters were considered such as the Henry's Law constant, heat of adsorption and pure component adsorption capacity. The measurements were performed by volumetric method at temperature above 100°C. The heat of adsorption was calculated by using equation 3.2 and was extrapolated to determine Henry's constant at ambient temperature.

The results of the experiment show that 5A and 13X zeolite has the highest Henry's constant and heat of adsorption among other adsorbents. Based on the pure component adsorption capacity, 13X zeolite has higher capacity compared to other adsorbents, thus was selected as the most suitable adsorbents for CO_2/N_2 separation. Unfortunately in their study, the adsorption isotherm measurement was only

measured for pressure below 2 bar. In this pressure region, the adsorption isotherm follows Henry's model. Most of the adsorbents have not yet reached the adsorption saturation yet at 2 bar pressure, thus the maximum capacity of the adsorbent cannot be determined. Henry's constant, heat of adsorption and capacity of 5A and 13X zeolite are shown in Table 2.1.

Hyung-wong et al. (2004) studied equilibrium and kinetic of CO_2 adsorption on 4A and CaX zeolite. The measurement was performed by gravimetric method and the results are shown in Table 2.1. The adsorption isotherm shows that the adsorbent is already saturated at 0.8 bar pressure. The adsorption isotherm of 4A zeolite follows Langmuir-Freindlich type while CaX zeolite follows Langmuir type. Their study has shown that 4A zeolite has higher capacity than CaX zeolite.

2.3 Methane Adsorption

Chihara et al. (1978) investigated the diffusivities of carbon molecular sieve for neon, argon, krypton, xenon, nitrogen, methane, ethylene, ethane, propylene, propane, n-butane, and benzene on CMS. The purpose of the study was to analyse the viability of natural gas component separation based on diffusivities. The measurement was performed by chromatographic method and the results are shown in Table 2.1. In their study the adsorption isotherm of CH_4 on CMS follows Henry's model.

Tezel and Apolonatos (1992) performed adsorption equilibrium measurement of CH_4, CO and N_2 gases on 4A zeolite, 5A zeolite and H-mordenite by chromatographic method. The purpose of the study was to determine the adsorption characteristic of those adsorbent and to study the viability of separating those gases. The adsorption isotherm was also determined in Henry's law region. The Henry's constant and heat of adsorption were determined in their study. Their experiment was performed at 263 to 333 K. The results of the study are shown in Table 2.1. From the results, H-mordenite has a far higher Henry's constant value compared to the other two adsorbents.

Triebe and Tezel (1996) studied the adsorption of methane, ethane, and ethylene on H-mordenite, 13X, 4A, and 5A zeolites. The main objective of their study was to

evaluate the viability of separating ethylene from light hydrocarbons. The adsorption isotherm was performed by chromatographic method at temperatures 233 to 473 K. The adsorption isotherm from this experiment follows Henry's model. The result of the experiment for CH_4 adsorption is given in Table 2.1.

Herbst and Harting (2002) measured the adsorption isotherm of supercritical fluid of argon, methane and nitrogen on activated carbon. The measurement was performed at pressure up to 500 bar by gravimetric method. The adsorption isotherm fit well with three parameter isothermal equation. The results show that the adsorption capacity of CH_4 decreases at very high pressure (higher than 60 bar). The contribution of the adsorbate volume was neglected in their study. Even though the volume of the adsorbate, attached to the adsorbent, was very small but at very high pressure the buoyancy effect is significant thus the measured weight is less than the actual weight. Detail explanation on the parameters considered in the adsorption isotherm measurement calculation for gravimetric method is given in chapter 3. Adsorption isotherm measurement that neglects the contribution of the adsorbate volume is known as Gibbs excess adsorption isotherm. On the other hand, the real adsorption isotherm that considers the effect of the adsorbate volume is known as absolute adsorption isotherm. Except in very extreme pressure, the absolute adsorption is equal to Gibbs excess adsorption. Most of the adsorption isotherms discussed in this review are based on Gibbs excess adsorption isotherm.

Dreisbach et al. (2002) calculated the maximum adsorption capacity of CH_4 on activated carbon using data from Herbst and Harting (2002), which is based on the absolute adsorption isotherm. The adsorption isotherm can be well represented by Langmuir type isotherm. The maximum adsorption capacity of CH_4 on activated carbon that is based on absolute adsorption isotherm is 9 mmol/g. The result from this experiment is given in Table 2.1.

Jayaraman (2003) studied the adsorption study on clipnotilolite, a varian of natural zeolite, for CH_4/N_2 separation. Beside pure clipnotilolite, ion exchanged clipnotilolite were also studied. Among the exchange ion used were Mg, Ca, Na, K, and Li. The adsorption isotherm and kinetic of CH_4 and N_2 on clipnotilolite were measured by volumetric method. The adsorption isotherm fit well with Langmuir

model. The results of the adsorption isotherm and kinetic measurement are shown in Table 2.1. However, a major disadvantage of using natural mineral as an adsorbent is the property of adsorbent depends on the location where the adsorbent is taken (Ruthven, 1988). In their study, the clipnotilolite was obtained from Spokane, USA.

2.4 Carbon Dioxide and Methane Adsorption

Rolniak and Kobayashi (1980) used chromatography method to measure the adsorption isotherm of pure methane and several methane-carbon dioxide mixtures on 5A and 13X zeolites. The measurement were performed at ambient temperature and at pressure up to 70 bar. The adsorption isotherm follows Ruthven's model. The results of these measurements are given in Table 2.1. From the result, it is observed that the capacity of CO_2 adsorbed on 13X zeolite is slightly higher than the 5A zeolite. However, the Henry's constant for both components was not determined in their study. For pure CH_4 adsorption, the experiment showed that the adsorption capacity of 13X zeolite was almost similar to 5A zeolite for pressure less than 30 bar. At 40 bar, 5A zeolite was already saturated with CH_4, while for 13X zeolite the adsorbent was not saturated even at 70 bar.

The binary adsorption mixture was performed from 0.77% to 5% CO_2 composition in the mixture. The result shows that at higher CO_2 concentration in the mixture, more CO_2 is adsorbed. At 5% CO_2 concentration in the mixture, the CO_2 adsorption capacity was only 5% different from a pure CO_2. It can be concluded that the presence of CH_4 in the mixture gives no significance effect to the adsorption capacity of CO_2 on 5A and 13X zeolites. The binary adsorption isotherm follows Ruthven's model.

Haq and Ruthven (1985) studied the adsorption of CH_4, CO_2, N_2, and O_2 in 4A and 5A zeolites by chromatographic method. The main purpose of the study was to identify the possibility of separating air and CH_4/N_2 mixtures at ambient condition. The adsorption isotherm parameter was presented in terms of Henry's constant and heat of adsorption. Similar to other chromatographic methods, the adsorption isotherm was measured in Henry's law region. In their study, Haq and Ruthven did

not produce any adsorption isotherm curves, therefore, the maximum capacity of the adsorbent cannot be determined. Beside the Henry's constant and heat of adsorption, they also studied the diffusivity coefficient for both adsorbents. However, the diffusivity coefficient for CO_2 and CH_4 on 5A zeolite cannot be calculated easily by chromatographic method since the diffusion was too rapid. The results of the experiment are shown in Table 2.1.

Dexin and Youfan (1987) studied the coadsorption of CH_4, C_2H_6, and CO_2 in 4A zeolite. The coadsorption breakthrough curves of those components were predicted theoretically by simulation and verified experimentally. The prediction was based on Ideal Adsorbed Solution Theory (IAST) method using single component adsorption isotherm data. The result shows that IAST model give good agreement with experimental data. The single component adsorption isotherm was obtained by gravimetric method at 30°C and can fit well with Langmuir model. The result of single component adsorption isotherm is shown in Table 2.1.

Beside those molecular sieve zeolites, carbon molecular sieve (CMS) also shows good potential to be used for CO_2 separation from natural gas. Kapoor and Yang (1989) identified potential application of carbon molecular sieve for CO_2/CH_4 separation. The adsorption isotherm and kinetic measurement were performed by volumetric method and the result are shown in Table 2.1. The adsorption isotherm shows good conformation with Langmuir model. It can be observed that the adsorption was based on kinetic mechanism since CO_2 diffuse 140 times faster than CH_4. The adsorbent has an enormous potential to be applied for landfill gas which contains 50% each of CO_2/CH_4 and tertiary oil recovery which contains 80% CO_2 and 20% CH_4. The dynamic adsorption studies using this adsorbent show that 90% purity of CH_4 can be obtained from 50% each of CO_2/CH_4 mixtures.

Vyas et al. (1994) studied the development of carbon molecular sieve (CMS), which was developed from coconut shell involving three main steps; pre-treatment, carbonization, and activation. The sample was characterized by BET, X-ray diffraction and scanning electron microscope. Four samples were produced in this experiment namely G1 to G4. The samples were used for adsorption isotherm and kinetic measurement of CO_2, C_2H_2, C_3H_6, CH_4, O_2, and N_2. The results of the

measurements are shown in Table 2.1. The adsorption isotherm follows Dubinin-Astakhov model.

The adsorption of methane, ethane, ethylene and carbon dioxide on silicalite-1 were investaged by Chaudary and Mayadevi (1996). The adsorption isotherm was measured by gravimetric method and the result is shown in Table 2.1. The Dubinin-Polanyi model fits the adsorption isotherm of CH_4 at 305 K; the Freundlich is found to fit the adsorption isotherm data of CH_4 at 353 K and CO_2 at 353 K; and the adsorption isotherm of CO_2 at 305 K follows Langmuir model. Due to its shape selectivity, Silicalite-1 could be a potential adsorbent for CO_2/CH_4 separation. However, this type of adsorbent is a newly developed material and not commercially available in the market.

Hernandez et al. (1997) studied adsorption of CO_2, CH_4, and N_2 in natural zeolites. The adsorption isotherm measurement was performed by using volumetric method at 17°C. They used erionite, mordenite and clipnotilolite as the adsorbents. The results indicate that erionite has the highest capacity among those adsorbents for both CO_2 and CH_4 adsorption. The adsorption capacity of CO_2 by natural zeolites in this research was also compared with the adsorption capacity of commercial activated carbon. The adsorption isotherm shows good conformation with Sips and Langmuir isotherm models. The adsorption of natural zeolite shows a higher capacity compared to the adsorption of commercial activated carbon because the surface of activated carbon is non-polar. Unfortunately, similar to hydrotalcite, the properties of the zeolite can vary depending on geographical location. The origin of the adsorbents used in their experiment was not mentioned.

The adsorption kinetic of CO_2, CH_4, and N_2 on activated carbon was experimentally investigated by Dreisbach et al. (1998). The kinetic measurement was performed by gravimetric method. Instead of measuring the diffusivity of the gas, the adsorption kinetic of the gases was investigated and compared with the time required for each gas to be adsorbed until the equilibrium condition was reached 1 mmol/g. The result show that CH_4 diffused faster than CO_2. Methane reached adsorption equilibrium within 605 seconds while CO_2 required 1222 seconds to reach

equilibrium. However, their study was not concerned with the adsorption isotherm measurement of the gases. The result of the measurement is shown in Table 2.1.

Nodzenski (1998) studied the adsorption of CO_2/CH_4 separation on activated carbon. His experiment was conducted by using volumetric method at pressure up to 60 bar and at two different temperatures, 288 and 298 K. The adsorption isotherm was described by thermal sorption equation in virial form. The result of the experiment is shown in Table 2.1. In comparison to molecular sieve adsorbents, activated carbon is not size selective for the separation of components. The pore size distribution of activated carbon is very wide. This condition is the main disadvantage of utilising activated carbon for natural gas purification. Since natural gas comprises many gases, instead of adsorbing CO_2 alone, other gases also will be adsorbed by the activated carbon. This will reduce the CO_2 adsorbing capacity of the adsorbent (Ruthven, 2005).

Pakseresht et al. (2002) conducted an equilibrium isotherm study on 5A zeolite. In this experiment, the measurement was performed for CO, CO_2, CH_4, and C_2H_4 by volumetric method. The adsorption isotherm data show good agreement with Sips and Langmuir model. The adsorption isotherm data show that 5A zeolite has high potential to be utilised for CO_2/CH_4 separation since CO_2 capacity on 5A zeolite is three times higher then CH_4. The adsorption capacity for CO_2 is already saturated at 20 bar while the adsorption capacity for CH_4 has not reached saturation even at 80 bar. The result of this experiment is given in Table 2.1.

Harlick and Tezel, (2002) investigated the separation of CO_2, CH_4, and N_2 gas on ZSM-5 with a SiO_2/Al_2O_3 ratio of 280. Both binary and pure adsorption isotherms of those gases were measured by chromatographic method. The pure isotherm follows Langmuir isotherm and the binary isotherm fitted well with Ideal Adsorption Solution Theory (IAST). It was very difficult to predict the maximum adsorption capacity since the adsorption isotherm measurement was performed at pressure below 1 bar. The result from this experiment is given in Table 2.1. Similar to silicalite-1, the ZSM-5 used in this work was custom made and not commercially available in the market

The binary adsorption measurement of CO_2 and CH_4 show that the CH_4 adsorption capacity reduced significantly as the CO_2 composition in the mixtures

increase. On the other hand, the CO_2 adsorption capacity did not change significantly as the CH_4 composition increased. This happens because CO_2 is very dominant and controls the adsorption isotherm of the binary system. Carbon dioxide and methane also competes to be adsorbed on the cationic site within the adsorbent structures. Carbon dioxide has higher polarity than CH_4, therefore it adsorbed stronger than CH_4 (Harlick and Tezel, 2002).

All the adsorption isotherm and kinetic studies are summarized in Table 2.1. All the Henry's constant in Table 2.1 were measured at 298 K or extrapolated to 298 K. Only the adsorption isotherm and kinetics parameter of CO_2 and CH_4 are shown here.

All the adsorption isotherm and kinetic studies are summarized in Table 2.1. All the Henry's contant in Table 2.1 were measured at 298 K or extrapolated to 298 K. Despite the adsorption measurements were also available for other gasses, only the adsorption isotherm and kinetics parameter of CO_2 and CH_4 are shown here.

Table 2.1 Summary of the literatures on adsorption-kinetic and equilibrium studies.

No	Researchers	Year	Measurement Method	Adsorbent	Adsorbate	Henry's constant (Dimensionless)	Henry's constant (mmol/gr/bar)	Capacity (mmol/g)	Diffusivity (cm^2/s)	Diffusivity Ratio	Diffusion Time Constant (1/s)	Adsorption Isotherm model
1	Chihara et al.	1978	Chromatographic	CMS	CH_4	-	-	-	$1.3x10^{-4}$		-	Henry's
2	Rolniak Kobayashi	1980	Chromatographic	5A Zeolite	CO_2	0.342	-	4.20	-	-	-	Ruthven
					CH_4	1.114	-	3.50	-	-	-	Ruthven
				13X Zeolite	CO_2	0.261	-	5.00	-	-	-	Ruthven
					CH_4	1.599	-	-	-	-	-	Ruthven
3	Haq Ruthven	1985	Chromatographic	5A Zeolite	CO_2	0.007	-	-	-	-	-	Henry's
					CH_4	0.036	-	-	-	-	-	Henry's
4	Haq Ruthven	1985	Chromatographic	4A Zeolite	CO_2	0.002	-	-	$1.5x10^{-8}$	-	-	Henry's
					CH_4	0.031	-	-	$4.47x10^{-8}$		-	Henry's
5	Dexin Youfan	1987	Gravimetric	4A Zeolite	CH_4	-	1.43	1.33	$1.08x10^{-7}$	-	-	Langmuir
					CO_2	-	35.97	3.48	$2.24x10^{-7}$	-	-	Langmuir
6	Yang	1988	Volumetric	CMS	CH_4	-	6.13	3.15	-	-	$5x10^{-6}$	Langmuir
					CO_2	-	1.17	1.92	-	-	$9x10^{-4}$	Langmuir
7	Tezel Apolonatos	1992	Chromatographic	4A Zeolite	CH_4	0.093	-	-	-	-	-	Henry's
				5A Zeolite	CH_4	0.036	-	-	-	-	-	Henry's
				H-mordenite	CH_4	2.889	-	-	-	-	-	Henry's
8	Vyas et al	1994	Volumetric	CMS G1	CO_2	-	-	1.41	-	3.7	-	Dubinin Astakhov
					CH_4	-	-	0.40	-	4.2	-	Dubinin Astakhov
				CMS G4	CO_2	-	-	2.05	-	10	-	Dubinin Astakhov
					CH_4	-	-	0.40	-	12	-	Dubinin Astakhov
9	Triebe Tezel	1995	Chromatographic	Activated carbon	CO_2	0.006	-	-	-	-	-	Henry's
						-	-	-				Henry's
10	Triebe Tezel	1996	Chromatographic	13X Zeolite	CH_4	0.043	-	-	-	-	-	Henry's
				CaX	CH_4	0.090	-	-	-	-	-	Henry's
				4A Zeolite	CH_4	0.098	-	-	-	-	-	Henry's
				5A Zeolite	CH_4	0.038	-	-	-	-	-	Henry's
11	Chaudary Mayadevi	1996	Gravimetric	Silicalite 1	CO_2	-	0.59	1.90	-	-	-	Henry's
					CH_4	-	-	1.20	-	-	-	Langmuir

Table 2.1 Summary of the literatures on adsorption kinetic and equilibrium studies (continued).

No	Researchers	Year	Measurement Method	Adsorbent	Adsorbate	Henry's constant (Dimensionless)	Henry's constant (mmol/gr/bar)	Capacity (mmol/g)	Difusifity (cm^2/s)	Diffusifity Ratio	Diffusion Time Constant (1/s)	Adsorption Isotherm model
12	Hernandez et al.	1997	Volumetric	Erionite	CO_2	-	0.10	3.04	-	-	-	Dubinin-polanyi
				Mordenite	CO_2	-	0.14	1.91	-	-	-	Langmuir and Sips
				Clipnotilolite	CO_2	-	0.19	1.77	-	-	-	Langmuir and Sips
				Erionite	CH_4	-	-	0.60	-	-	-	Langmuir and Sips
				Mordenite	CH_4	-	-	0.40	-	-	-	Langmuir and Sips
				Clipnotilolite	CH_4	-	-	0.30	-	-	-	Langmuir and Sips
13	Dreisbach et al.	1998	Gravimetric	Activated carbon	CO_2	-	-	-	-	-	-	Langmuir and Sips
					CH_4	-	-	-	-	-	-	Not determined
14	Nodzenki	1998	Volumetric	Activated carbon	CO_2	-	-	7.14	-	-	-	Not determined
					CH_4	-	-	1.79	-	-	-	Virial Thermal sorption
15	Ding	1999	Dynamic Column Breakthrough	Hydrotalcite	CO_2	-	-	0.58	-	-	-	Virial Thermal sorption
16	Sriwardani et al.	1999	Volumetric	13X Zeolite	CO_2	-	-	6.50	-	-	-	Langmuir
				Activated carbon	CO_2	-	-	8.00	-	-	-	Langmuir
17	Herbst Harling	2002	Gravimetric	Activated carbon	CH_4	-	-	8.70	-	-	-	Not determined
18	Dreisbach et al.	2002	Gravimetric	Activated carbon	CH_4	-	-0.57	10.79	-	-	8.70	Not determined Three parameter
19	Pakseresh et al.	2002	Volumetric	5A Zeolite	CO_2	-	0.08	3.90	-	-	10.79	Three parameter Langmuir
					CH_4	-	0.01	2.03	-	-	-	Langmuir
20	Harlick Tezel	2002	Chromatographic	ZSM-5-280	CO_2	2.996	-	4.30	-	-	-	Langmuir and Sips
					CH_4	0.724	-	4.60	-	-	-	Langmuir

Table 2.1 Summary of the literatures on adsorption kinetic and equilibrium studies (continued).

No	Researchers	Year	Measurement Method	Adsorbent	Adsorbate	Henry's constant (Dimensionless)	Henry's constant (mmol/gr/bar)	Capacity (mmol/g)	Difusifity (cm^2/s)	Diffusifity Ratio	Diffusion Time Constant (1/s)	Adsorption Isotherm model
21	Hyungwong et al.	2004	Gravimetric	4A Zeolite	CO_2	-		5.06	-	-	-	Langmuir
				CaX	CO_2	-	24.94	3.24	-	-	$3.64x10^{-5}$	Langmuir-Freundlich
22	Jayaraman et al.	2004	Volumetric	Purified clipnotilolite	CH_4	-	1.85	-	-	-	$3.74X10^{-3}$	Langmuir
				Mg-clionotilolite	CH_4	-	1.94	-	$2x10^{-5}$	-	-	Langmuir
				Ca-clipnotilolite	CH_4	-	0.25	-	$6x10^{-5}$	-	-	Langmuir
				Na-clipnotilolite	CH_4	-	0.05	-	$1.1x10^{-3}$	-	-	Langmuir
				K-clipnotilolite	CH_4	-	0.80	-	$4.1x10^{-4}$	-	-	Langmuir
				H-clipnotilolite	CH_4	-	0.80	-	$5.8x10^{-4}$	-	-	Langmuir
				Li-clipnotilolite	CH_4	-	2.12	-	$3.2x10^{-2}$	-	-	Langmuir
				Mg/Ca (20/80) clipnotilolite	CH_4	-	1.87	-	$3.8x10^{-4}$	-	-	Langmuir
				Mg/Ca (50/50) clipnotilolite	CH_4	-	1.12	-	$6.5x10^{-4}$	-	-	Langmuir
				Mg/Ca (80/20) clipnotilolite	CH_4	-	2.00	-	$6.5x10^{-3}$	-	-	Langmuir
				K/Na (20/80) clipnotilolite	CH_4	-	1.63	-	$6.9x10^{-3}$	-	-	Langmuir
				K/Na (50/50) clipnotilolite	CH_4	-	2.07	-	$1.4x10^{-4}$	-	-	Langmuir
				K/Na (80/20) clipnotilolite	CH_4	-	1.87	-	$2.2x10^{-4}$	-	-	Langmuir
				Mg/Na (20/80) clipnotilolite	CH_4	-	0.79	-	$3.2x10^{-4}$	-	-	Langmuir
				Mg/Na (50/50) clipnotilolite	CH_4	-	0.70	-	$4.5x10^{-5}$	-	-	Langmuir
				Mg/Na (80/20) clipnotilolite	CH_4	-	1.85	-	$9.x10^{-5}$	-	-	Langmuir
23	Harlick Tezel	2004	Volumetric	5A Zeolite	CO_2	-	586.19	-	$2.x10^{-5}$	-	-	Langmuir
				13X Zeolite	CO_2	-	254.86	3.20		-	-	Henry's

Several conclusions can be withdrawn from Table 2.1. The Henry's constant obtained from chromatographic method has different unit compared to other measurement methods. The adsorption isotherm in chromatographic method is expressed as the adsorbate concentration in adsorbent against concentration of the adsorbate in gas phase. In chromatographic method, the Henry's constant was obtained from the analytical solution of Laplace domain and has no unit. Detail calculation procedures of chromatographic method are available in many literatures and also in adsorption handbooks such as by Do, (1998). It is not possible to convert the Henry's constant obtained from other methods to dimensionless form since information of the pore volume of the adsorbent, which is required to calculate the concentration of the adsorbate in adsorbent phase, are not provided by the literature. Therefore, it is very dificult to compare the results performed by chromatographic method to other measurement methods.

Based on Table 2.1, the adsorption measurement performed by the same method can give different results. This can be observed from the result given by Tezel and Apolonatos, (1992) and Haq and Ruthven, (1985) for the measurement of Henry's constant of CH_4 adsorption on 4A zeolite. The Henry's constant obtained by Tezel and Apolonatos was three times higher than the Henry's constant obtained by Haq and Ruthven. Another example is the results produced by Pakseresh et al., (2002) and Herlick and Tezel, (2004) for the measurement of Henry's constant of CO_2 adsorption on 5A zeolite by volumetric method. Harlick and Tezel performed the experiment at temperatures above 100°C and Henry's constant obtained from the measurement was extrapolated to ambient temperature. The result shows that the Henry's constant ratio obtained from Herlick and Tezel measurement was 750 times higher than the result obtained by Pakseresh et al. This shows that temperature has significant contribution to the adsorption measurement. Extrapolation from different operating condition may give different result.

Equilibrium and kinetic information are required in order to determine the mechanism controls the adsorption process. The parameters required to determine the adsorption mechanism are the Henry'constant, maximum capacity and diffusivity (Yang, 2002; Ruthven, 1988). From Table 2.1, it can be observed that only Kapoor and Yang, (1989),

Dreisbach et al. (2002), and Hyungwong et al.(2004) have calculated all three variables. Among them only Kapoor and Yang, (1989) calculated those parameters for both CO_2 and CH_4 adsorption on CMS . Similar measurement for zeolite based materials have not been explored so far.

Gravimetric method, especially with the availability of magnetic suspension balance, provides more accurate result compared to other adsorption isotherm measurement methods. The comparison of the adsorption measurement methods is given in Chapter 1. It can be observed from Table 2.1 that, despite its potential application, the measurement of zeolite based materials for CO_2 and CH_4 adsorption using gravimetric adsorption isotherm measurement is very rare. Most of the studies were focused on activated carbon adsorption. Based on the current literature in gravimetric measurement, the best adsorbent for CO_2/CH_4 separation has not yet been identified.

From Table 2.1, most of the adsorbents measured by chromatographic method follow Henry's isotherm. This is because the measurement was performed at low pressure. At low pressure, Henry's law is dominant whereby additional pressure will linearly increase the adsorbent capacity. Most of the measurements that were performed by volumetric or chromatographic method follow Langmuir isotherm. In some cases, the adsorption isotherm not only follows langmuir isotherm but also can be represented by Sips equation as well (Hernandez et al. 1997 and Pakseresh at al. 2002). Some other adsorption isotherm model such as Dubinin-Polanyi, Ruthven, and three parameter model were also used but to a lesser extent.

All the adsorbents given in Table 2.1 have the potential to be used in CO_2/CH_4 separation. However, based on technical and economical considerations, not all of the adsorbents are suitable for commercial application. Natural zeolites such as mordenite, clipnotilolite, erionite, and hydrotalcite are not suitable for large scale commercial application because the physical properties of the products are not homogeneous and depend on the geographical location of origin (Ruthven, 1988). Availability of the adsorbent material is also an important consideration in commercial application. Therefore, despite their potential application, custom mades material that are not commercially available such as ZSM 5-280 and silica-1 are not suitable for commercial application. Although activated carbon has high adsorption capacity, it is not shape

selective adsorbent. Therefore activated carbon is capable of adsorbing most of the components in natural gas, hence reducing the adsorption capacity for CO_2. Based on the above reasons, only 4 of the adsorbents are identified as potential adsorbents for CO_2/CH_4 separation, namely 4A zeolite, 5A zeolite, 13X zeolite, and CMS.

2.5 Parametric Study

Basmadjian, (1975) was among the earliest researcher who investigated the effect of operating conditions on process performance. He studied the effect of regeneration temperature on cooling down period. The adsorption and regeneration of CO_2 adsorption in He carrier gas on 5A zeolite was studied. He found that long cooling down period was the major disadvantage of Temperature Swing Adsorption (TSA) process. Higher regeneration temperature resulted in longer cooling down period. He suggested that under the following criteria, the cooling down step is not required.

$$\frac{n_f}{y_f} > \frac{Cp_s}{Cp_g} \text{ and } \frac{n_p}{y_f} > 1.5\frac{Cp_s}{Cp_g} \tag{2.1}$$

where n_f, y_f, Cp_s, Cp_g, and n_p are equilibrium amount at feed temperature, mole fraction of adsorbate in the fluid phase, heat capacity of solid, heat capacity of the carrier gas, equilibrium amount at characteristic temperature (T_p) repectively. The characteristic temperature (T_p) can be obtained from the equation given below:

$$T_p = T_{feed} - \frac{n_f \Delta H}{Cp_g(n_f / y_f) - Cp_s} \tag{2.2}$$

where ΔH is the heat adsorption. However, equation 2.1 neglects the contribution of the adsorbate heat capacity. The adsorbate heat capacity should be included at higher concentration, such as in bulk separation since the effect of adsorbate concentration can be very high.

Cen and Yang, (1986) studied the bulk separation of a five-component mixtures of coal gasification product on activated carbon. The components were CO, CO_2, CH_4, H_2, and H_2S. The main objective of their study was to obtain pure H_2 product with low concentration of CO_2 and H_2S from the product of a steam reformer. The effect of the end pressure of blow down step, feed flow rate, and feed pressure to the product purity were

also studied. The results show that at lower pressure of blow down step, the product purity and recovery increased. The pressure effect study, except for H_2S, shows that the purity of the product increased as the pressure increased. A similar pattern was also observed in flow rate effect study. Except for H_2S, the purity of all other four components increased as the flow rate increased.

Kapoor and Yang, (1989) investigated the separation of CO_2/CH_4 mixtures on CMS. The study shows that the separation was based on kinetic mechanism where CO_2 diffused faster than CH_4 onto CMS. The effect of cycle time, feed pressure, and evacuation pressure to CH_4 purity and recovery were studied. They found that there was an optimal cycle time that yielded maximum purity and recovery. Longer cycle time gave enough time for both components to reach equilibrium, thus the kinetic separation cannot be achieved. On the other hand, at shorter cycle time, the CO_2 was not completely adsorbed, thus the CH_4 product had high concentration of CO_2. A similar trend was also observed for the effect of pressure to purity and recovery. High purity and recovery were observed at optimum pressure condition. The evacuation pressure study shows that lower evacuation pressure produced high purity product without significant changes in recovery. The separation had successfully achieved 90% of CH_4 purity and over 90% of CH_4 recovery at feed throughput of 140L/h/kg sorbent at ambient temperature and pressure.

Parametric analysis of thermal swing cycle for multicomponent adsorption was reported by Huang et al. (1989). They investigated the adsorption of ethane, propane, and their mixtures on activated carbon. The effects of several parameters in adsorption and regeneration steps were studied. In the adsorption step, the effect of carrier gas, feed concentration, velocity, pressure, and initial bed temperature to break through time were investigated. The results show that helium was relatively unadsorbed thus more suitable to be used as regenerant compare to nitrogen. At higher concentration of more strongly adsorbed component (in this case propane) the break through time reduced significantly. Similar trend was also observed for the effect of velocity and pressure. Higher propane velocity and partial pressure reduced the breakthrough time significantly whereby initial bed temperature did not give any significant impact to the breakthrough time.

For regeneration study, Huang et al. (1989) studied the effect of purge gas, regenerant velocity, regeneration temperature, and initial bed loading to depletion time. Depletion time in regeneration study is similar to breakthrough time in adsorption study, which is defined by Schork, (1986) as the time required to clean minimal 99% of the adsorbate on the adsorbent. It was shown that nitrogen can regenerate the bed faster than helium due to its higher heat capacity. At higher regenerant velocity, the depletion time decreased. The depletion time was also reduced as the regenerant temperature increased. It was observed that the depletion time was not significantly affected by the initial loading. The effect of regeneration temperature to the energy requirement was also studied. The energy requirement consists of the energy required to blow the purge gas and the energy required by the heater to increase the bed and purge gas temperatures. At high temperature, energy required by the heater increased but the energy required to blow the gas decreased since the column was regenerated faster. An optimum temperature that yielded minimum energy requirement was also observed.

Farooq and Ruthven, (1992) studied the production of nitrogen via air adsorption on CMS. The pressure effect to nitrogen purity and recovery was analyzed. The result concluded that as the pressure increased, the nitrogen purity increased, while the recovery decreased. At 6 bar, the nitrogen purity can reach 97 % while the recovery was only 40%. Since the air price is very cheap, this low recovery is acceptable.

Diagne et al. (1995) studied the separation of CO_2 from air on 13X zeolite. The effect of several operating procedures such as feed concentration, stripping reflux ratio, and the ratio of adsorption to purging pressure were experimentally investigated. Their finding shows that higher CO_2 concentration reduces air purity. Reflux ratio is the ratio of the product that is being used to regenerate the column to the total product. An optimal reflux ratio was observed at 0.6-0.8 with maximum air purity achievable to 99%..The product purity was significantly improved for pressure ratio below 5. At pressure ratio above 5, the purity of the product only increased slightly. This observation was mainly due to the adsorption characteristic that followed Langmuir equation. However, after the adsorption plateau was reached further pressure increment did not significantly increase the adsorption capacity.

Fatehi et al. (1995) studied the separation of 60%-40% and 92%-8% of methane-nitrogen mixtures on CMS. Their studies were focused on the effect of cycle time, velocity and purge to feed ratio to methane purity in the product. At 60% methane concentration in the feed, a product purity up to 76% methane was obtainable, whereby at 92% methane concentration the product purity can reach up to 98%. An optimum velocity and cycle time were obtained for a set of operating conditions. One cycle consists of a series of following steps i.e. feed, blow down, purge, and repressurization. The effect of purge to feed ratio cannot be observed since most of the cycle time was also changed when the purge to feed ratio was varied.

The sensitivity of adsorption capacity on temperature was investigated by Talu et al. (1996). The research was performed for air separation on 5A zeolite. The results indicate that the adsorbent capacity was reduced by 25% with 20°C temperature increment. In this system, the cooling down period was unavoidable.

The effect of adsorption pressure and composition on methane purity, for CH_4/N_2 separation on CMS was studied by Warmuzinki and Sodzawiczny, (1998). They obtained an optimum pressure and feed composition that yielded highest methane purity. At higher CH_4 composition in the feed, the purity of the methane decreased as the pressure increased. However for less than 20% CH_4 concentration in the feed, the methane purity was increased as the pressure increased.

Doong and Propsner, (1998) published an experimental study of the effect of process symmetry on oxygen purity for air separation on 5A zeolite. In their study, two beds were used with one for adsorption while another for regeneration. Both experimental and simulation results indicated that the product purity was significantly reduced when there was more than 10% cycle time difference between the adsorption and regeneration step.

Silva et al. (2000) studied the separation of n-paraffin and iso-paraffin by 5A zeolite. n-parafin was adsorbed on the adsorbent due to its smaller molecular size while the branched isomers were excluded. The effect of purge to feed mole ratio on iso-parafin purity and recovery was also analyzed. The purity of iso-paraffin increased as the purge to feed ratio was increased. At a purge to feed ratio of 0.25, purity of iso-paraffin reached 100 % while the recovery was 70%.

Waldron and Sircar, (2000) carried out research on PSA process for the production of high purity hydrogen from binary hydrogen/methane mixture on activated carbon. The influences of several variables such as feed pressure, feed composition, and purge gas pressure on purity and recovery were investigated. They concluded that the H_2 productivity increases as the pressure increases. There was also an optimum pressure range that gave highest recovery. H_2 recovery was not significantly affected by the feed composition but the productivity increased significantly as the H_2 composition in the feed was increased. Both productivity and recovery of H_2 were reduced as the purge gas pressure increased.

The performance of PSA process for oxygen separation from air by using 13X zeolite was investigated by Shin et al. (2000). The effect of pressurization step time and equalization step time to oxygen productivity and recovery were analyzed in this study. This experiment was performed at 3.2 atm and the result shows that as the pressurization step time increases, the productivity and recovery of the oxygen increase. However, after certain pressurization time, the recovery and productivity practically remain constant. The oxygen recovery remains constant after 30 seconds while the oxygen productivity remains constant after 40 seconds. The effect of equalization step time shows similar behavior with the effect of pressure step time.

Mendes et al. (2001) also investigated the oxygen separation from air. In their study, 5A zeolite was used as the adsorbent. The effects of adsorption pressure, purge and product flow rate, and cycle time on oxygen purity and recovery were evaluated. The results show that both oxygen purity and recovery decreases as the adsorption pressure increases. On the other hand, the product purity decreases while the recovery increases as the flow rate increases. A similar trend was also observed in cycle time effect study. As the cycle time increases, the product purity decreases while the recovery increases. In purge flow rate effect study, the result shows that both product purity and recovery decrease as the purge flow rate increases.

The adsorption performance of a ternary mixture of benzene, toluene, and *p*-xylene on activated carbon was studied by Daeho Ko et al. (2001). The influence of purge gas temperature to depletion time, cyclic operating step time, purge gas consumption, and regeneration energy requirement were the main concern in their study. They found that

high purge gas temperature yields high roll-up and short depletion time. Roll-up condition means the situation where the flow rate of the adsorbed component at regeneration step is higher than the flow rate of the component at adsorption. This condition basically exists in initial period of regeneration step and the flow rate is eventually reduced to zero with time. The cyclic operating step time is mainly influenced by the time required to cool down the bed. The cool down time increases as the purge temperature increases. Based on equation 2.1, at temperatures below 415 K the bed does not require cooling down. Both purge gas and regeneration energy required decrease as the regeneration temperature increases. The energy requirements consist of energy required to blow the purge gas and energy required by the heater to increase the purge gas and the bed temperature. However at more than 415 K, the decrement of the regeneration energy is not significant.

Serbezov, (2001) studied the effect of adsorption pressure on the length of Mass Transfer Zone (MTZ). The MTZ is the zone where the adsorption takes place. It has a trailing edge where the adsorbent is already equilibrated and a leading edge where the adsorbent is still unutilized. However, the MTZ cannot be measured directly and can only be predicted by modeling. In PSA, the initial MTZ is generated at pressurization step. By increasing the pressure as rapid as possible, the initial MTZ length can be reduced. Even though the pressurization step has significant effect on MTZ length, the adsorption pressure itself has no significant effect on the MTZ length. Nevertheless, it is not common to analyze the performance of the system based on MTZ in industrial application.

Cruz et al. (2002) developed model for oxygen separation from air on a commercially available molecular sieve. The effect of pressure, pressurization time, adsorption time, adsorbent size and bed temperature on purity and recovery were simulated. The simulation results show that, pressure increment leads to an enhancement of process performance, since purity increases while recovery remains unchanged. However, the purity increment was more significant at lower pressure. A similar trend was also observed in the pressurization time effect study. The increment of pressurization time decreases oxygen purity. However, an optimum pressurization time that yielded highest recovery was observed. For adsorption time effect study, an optimal adsorption time that

yielded highest purity and recovery was observed. The adsorbent size effect is conversely related to the effect of pressure drop. As pressure drop increases the adsorbent size decreases. The simulation results also show that as the pressure drop increased, oxygen purity increases while the recovery decreases. Similar to the results of Basmadjian, (1975), Huang and Fair, (1989), and Talu, (1996), the purity and recovery of the bed decreases as the bed temperature increases. Therefore, increasing the overall heat transfer of the bed can increase the purity of the product.

Carbon dioxide removal from flue gas by adsorption on 13X zeolite was investigated by Gomes and Yee, (2002). The effect of feed flow rate, process cycle time, and inert composition in the feed on purity and recovery were analyzed. The study shows that the feed flow rate and the inert gas composition affect the purity and recovery in a similar trend. Increasing the flow rate or composition of inert gas in the feed leads to a decrease on N_2 purity but an increase on N_2 recovery. The cycle time effect study shows that as the cycle time increase the purity also increases with a slight decrease in recovery.

Similar to Gomes and Yee (2002), removal of CO_2 from air by PSA was also studied by Fang et al. (2003). The adsorption was also performed on 13X zeolite and the effect of cycle time, ratio of regenerant to feed velocity, velocity of regenerant and pressure ratio on air purity was analyzed. The study shows that the purity of the product remained constant before the cycle time reached 20 minutes. After the cycle time has reached 20 minutes, the purity of the air decreased significantly. Based on the velocity ratio effect study, the air purity increases as the ratio of regenerant to feed velocity decreases. The increment was more obvious at lower velocity ratio. The regenerant velocity ratio effect study shows that, at a constant velocity ratio, the increment of regenerant velocity significantly reduced the air purity. The pressure ratio affects air purity inthe same patern as velocity ratio. The increase in the pressure ratio conduces to an increase in air purity.

Yuwen et al. (2004) performed an experimental study of oxygen production from air by adsorption. In this study, 5A zeolite was selected as the adsorbent. The effect of adsorption pressure and purge gas quantity to oxygen productivity and purity were investigated. They identified that the oxygen productivity remain constant for the whole operating condition. However, an optimal operating pressure was observed at 1.8-2.1 bar. Neither higher nor lower pressure from this range will reduce the oxygen purity. They

also found that the higher purge gas quantity increases the product purity but reduces the oxygen productivity since more oxygen is used to regenerate the column.

Chou and Chen (2004) studied the separation of CO_2 from flue gas by using 13X zeolite. The influence of cocurrent depressurization time, continuous feed time, and feed pressure to purity and recovery were analyzed in this experiment. Cocurrent depressurization is similar with blow down step except the flow direction is inline with the feed direction. The result indicated that the purity of the product increases as the cocurrent depressurization time increases. On the other hand, the recovery decreases as the cocurrent depressurization time increases. Continuous feed time has the same effect on purity and recovery as cocurrent depresurrization time. As the continuous feed time increases, flue gas purity increases but the recovery decreases. Based on the pressure study, the pressure increment leads to an increase in purity but a decrease in recovery. Nevertheless, at pressure higher than 1.5 bar both purity and recovery are constant.

Clausse et al. (2004) investigated the separation of C_2H_4, CO_2, and N_2 on activated carbon. Ethane and cabon dioxide was coadsorbed in this experiment and pure N_2 was produced. The effect of initial bed temperature and feed temperature to breakthrough time were studied. The experimental results indicate that the initial bed temperature tend to reduce the breakthrough time while the feed temperature practically does not affect the breakthrough time.

Jee et al. (2004) studied oxygen purification from a ternary mixture of O_2, N_2, and Ar by adsorption on CMS. The effect of nitrogen composition on oxygen purity and recovery was studied. Based on this experiment, as the nitrogen composition in the mixture increases, the oxygen purity decreases without any significant changes on oxygen recovery.

A summary of the review on parametric analysis in adsorption system and operating conditions is given in Table 2.2.

Table 2.2 Summary of the literature on parametric analysis study.

No	Researchers	Year	Adsorbent	Adsorbate	Operating Parameter	Performance Criteria	Operating Parameter Influences
1	Basmadjian	1975	5A Zeolite	CO_2	1.Temperature	Cooling time	The cooling down period increases as the regeneration temperature increases
2	Cen Yang	1986	Activated carbon	CO_2 CO CH_4 H_2S	1.Pressure	Purity Recovery	Except for H_2S, the purity increases as the pressure increases
					2.Flow rate	Purity Recovery	Except for H_2S, the purity increases as the flow rate increases
					3. Blowdown Pressure	Purity Recovery	The purity and recovery increase as the. blowdown pressure reduces
3	Huang & Fair	1989	Activated carbon	C_2H_6 C_3H_8	1. Carrier gas	Breakthrough time	Helium has shorter breakthrough time compare to nitrogen.
					2. Feed concentration	Breakthrough time	The breakthrough time will increase as the key component concentration increases
					3. Velocity	Breakthrough time	The breakthrough time will increase as the key component velocity increases
					4. Initial bed temperature	Breakthrough time	Initial bed temperature gives no significant effect to break through time
					5. Bed pressure	Breakthrough time	The breakthrough time will increase as the key component partial pressure increases
					6. Regenerant	Depletion time	Nitrogen has shorter depletion time compare to helium
					7. Regenerant velocity	Depletion time	The depletion time will increase as the regenerant velocity increases
					8. Regeneration temperature	Depletion time	The depletion time will increase as the regenerant temperature increases
					9. Initial bed loading	Depletion time	Initial bed loading has no significant effect to depletion time
4	Kapoor Yang	1989	CMS	CO_2 CH_4	1.Cycle time	Purity Recovery	An optimum cycle time which yielded higher purity and recovery was observed.
					2. Pressure	Purity Recovery	An optimum pressure which yielded higher purity. and recovery was observed
					3.Evacuation Pressure	Purity Recovery	Purity increases while recovery remains constant as the evacuation pressure decreases

Table 2.2 Summary of the literature on parametric analysis study (continued).

No	Researchers	Year	Adsorbent	Adsorbate	Operating Parameter	Performance Criteria	Operating Parameter Influences
5	Farooq Ruthven	1992	CMS	Air	1. Pressure	Purity Recovery	Purity increases while the recovery decreases as the pressure increases
6	Diagne et al.	1995	13X Zeolite	CO_2 Air	1. Feed concentration	Purity	Purity decreases as the adsorbate concentration increases
					2. Stripping reflux ratio	Purity	An optimum striping reflux ratio that yielded higher purity was observed
					3. Pressure ratio	Purity	Purity increases as the pressure increases; at pressure ratio above 5, the purity increment is not significant.
7	Fatehi et al.	1995	CMS	CH_4	1. Concentration	Purity	Purity increases as the concentration increases
					2.Half cycle time	Purity	An optimum cycle time that yielded higher purity was observed
					3.Velocity	Purity	An optimum velocity that yielded higher purity was observed
					4.Purge to feed ratio	Purity	Purge to feed ratio effect can not be observed
8	Talu et al.	1996	5A Zeolite	Air	1.Temperature	Capacity	Adsorbent capacity decreases as bed temperature increases
9	Doong Propsner	1998	5A Zeolite	Air	1. Process Symmetry	Purity	Purity decreases significantly for more than 10% step time difference,
10	Warmuzinki Sodzawicny	1998	CMS	CH_4 N_2	1.Adsorption Pressure	Purity Recovery	An optimum pressure that yielded higher purity d and recovery was observe
					2. Concentration	Purity Recovery	An optimum concentration that yielded higher purity and recovery was observed
11	Waldron Sircar	2000	Activated carbon	H_2 CH_4	1.Pressure	Recovery Productivity	An optimum pressure that yielded higher recovery was observed Productivity increases as pressure increases
					2.Composition	Recovery Productivity	Productivity increases, recovery remains. constant as the composition increases
					3.Purge gas pressure	Recovery Productivity	Purity and recovery increase as purge gas pressure increases

Table 2.2 Summary of the literature on parametric analysis study (continued).

No	Researchers	Year	Adsorbent	Adsorbate	Operating Parameter	Performance Criteria	Operating Parameter Influences
12	Mendes et al.	2000	5A Zeolite	Air	1. Pressure	Purity Recovery	Purity and recovery decrease as the pressure increases
					2.Flow rate	Purity Recovery	Recovery increases while purity decreases as flow rate increases
					3.Purge flow rate	Purity Recovery	Purity and recovery decrease as the purge flow rate decreases
					4. Cycle time	Purity Recovery	Purity decreases while recovery increases as the cycle time increases
13	Ko et al.	2001	Activated carbon	Benzene Toluene p-xylene	1.Purge gas temperature	Depletion time	Depletion time decreases as the purge gas temperature increases
						Cyclic time	Cyclic time increases as the purge gas temperature increases
						Purge gas consumption	Purge gas consumption decreases as the purge gas temperature increases
						Energy requirement	Energy requirement decreases as the purge gas temperature increases
14	Serbezov	2001	(modeling)	(modeling)	1.Adsorbent Selectivity	Length of MTZ	Length of MTZ increases as the adsorbent selectivity increases; however, if the selectivity is higher than eight, The length of MTZ is constant
					2. Adsorption pressure	Length of MTZ	Adsorption pressure has no significant effect on the length of MTZ
					3. Pressurization time	Length of MTZ	Length of MTZ decrease as pressurization time increases
15	Cruz et al.	2002	CMS	N_2	1.Pressure	Purity Recovery	Purity increases while recovery remains constant as the pressure increases
					2.Pressurization time	Purity Recovery	Purity decreases as the pressurization time increases; an optimum pressurization time that yielded higher recovery was observed
					3.Adsorption time	Purity Recovery	An optimum adsorption time value that yielded optimum purity and recovery was observed

Table 2.2 Summary of the literature on parametric analysis study (continued).

No	Researchers	Year	Adsorbent	Adsorbate	Operating Parameter	Performance Criteria	Operating Parameter Influences
15	Cruz et al.	2002			4.Adsorbent size	Purity Recovery	Purity decreases while recovery increases as the adsorbent size increases
					5.Bed temperature	Purity Recovery	Purity and recovery decrease as the bed temperature decreases
16	Gomes Yee	2002	13X Zeolite	CO_2	1.Flow rate	Purity Recovery	Purity decreases while recovery increases as the flow rate increases
					2. Cycle time	Purity Recovery	Purity increases while recovery decreases as the cycle time increases
					3. Inert gas content	Purity Recovery	Purity decreases while the recovery increases as the inert gas composition increases
17	Fang et al.	2003	13X Zeolite	CO_2	1.Cycle time	Purity	Cycle time has no significant effect to purity; however, after 20 minutes purity will decrease significantly
					2.Ratio of regenerant to feed velocity	Purity	Purity decreases as the ratio of regenerant to feed velocity decreases
					3.Regenerant velocity	Purity	Purity decreases as the regenerant velocity increases
					4.Pressure ratio	Purity	Purity decreases as the pressure ratio increases
18	Clausse et al.	2004	Activated carbon	CO_2 C_2H_4	1.Feed temperature	Breakthrough time	Feed temperature has no significant effect on break through time
					2.Initial bed temperature		Breakthrough time decreases as initial bed temperature increases
19	Chou Chen	2004	13 X zeolite	CO_2	1.Cocurrent depressurization time	Purity Recovery	Purity increases while recovery decreases as the cocurent depressurization time increases
					2.Cycle time	Purity Recovery	Purity increases while recovery decreases as the cycle time increases
					3.Feed pressure	Purity Recovery	Purity increases while recovery decrease as the pressure increases; however, at pressures higher than 1.5 bar both purity and recovery are constant

Table 2.2 Summary of the literature on parametric analysis study (continued).

No	Researchers	Year	Adsorbent	Adsorbate	Operating Parameter	Performance Criteria	Operating Parameter Influences
20	Yuwen et al.	2005	5A Zeolite	N_2	1.Pressure	Productivity Purity	An optimum pressure that yielded higher purity was observed. Pressure has no significant effect on productivity
					2.Purge quantity	Productivity Purity	Purity increases while productivity decreases as the purge gas quantity decreases
21	Jee et al.	2004	CMS	N_2	1.N_2 composition	Purity Recovery	Purity decreases while the recovery remains constant as N_2 composition increases

From Table 2.2, it is noticed that the parametric study of CH_4/CO_2 adsorption is very scarce. Up till now only Kapoor and Yang (1989) studied parametric analysis of CO_2/CH_4 adsorption on CMS. The separation in their system was based on kinetic mechanism. Beside CMS, zeolite based adsorbent such as 4A, 5A and 13X zeolite show good potential as the adsorbent for CO_2/CH_4 separation. The parametric study on other adsorption system not necessarily gives similar pattern. Therefore, the parametric study of CO_2/CH_4 is vital to identify the best adsorbent.

Based on Table 2.2, it can be concluded that some parameters can be optimized in order to obtain the optimum operating condition for better performance, while others only show pattern. For example, Cen and Yang, (2006) who studied the effect of blow down pressure on purity and recovery found that lower blow down pressure will increase purity and recovery. In this case, higher purity and recovery can be achieved by simply reducing the blow down pressure. On the other hand, Kapoor and Yang, (1989) investigated the effect of pressure on purity and recovery. They found that there is a certain pressure that can yield higher purity and recovery. Determination of that pressure value is very important in order to obtain optimum system performance. The performance of a system can be evaluated based on purity, recovery, capacity, breakthrough time, and productivity. However, most of researchers evaluated the system performance based on purity and recovery.

The effect of an operating condition to purity and recovery can have opposite result. Farooq and Ruthven, (1992) analyzed the effect of adsorption pressure on purity and recovery. Based on their study, purity of the product is increases while recovery decreases as pressure increases. In a natural gas purification system, the CO_2 content should be lower than 2%. Based on Farooq and Ruthven result, the purity of natural gas can be increased by applying high adsorption pressure. However, purity increment after the CO_2 concentration in the stream has been reduced to less than 2% is no longer required. Any pressure increment after this purity level will only reduce the recovery of natural gas. Based on the above case, an optimum operating condition that yields high recovery at acceptable purity has to be determined.

Among those operating conditions studied so far, some operating conditions have an optimum value that yield better system performance. Among those operating conditions

that could have an optimum value are pressure, flow rate, composition, cycle time, temperature, purge gas pressure, purge quantity, evacuation pressure, and stripping reflux ratio. The cycle time and velocity depends on the adsorption flow rate. Higher adsorption flow rate will reduce the cycle time and increase the velocity. Therefore, the effect of cycle time and velocity on the system performance can also be studied by analyzing the effect of the flow rate to the system performance. The effects of purge gas pressure, purge quantity, evacuation pressure, and stripping reflux on purity for CO_2/ CH_4 adsorption are also important. However, these parameters are not within the scope of the study here. Therefore, in this research only the effect of pressure, flow rate, composition, and temperature on purity and recovery are studied.

2.6 Concluding Remarks

From the review of adsorption isotherm and kinetic measurements of CO_2 and CH_4, the following conclusions can be withdrawn:

1. The adsorption isotherm data from chromatographic method for the same adsorbent and operating condition may give different results from other methods.
2. The measurements performed by the same researchers can give different results due to different of operating condition.
3. Only Kapoor and Yang, (1989) have measured the most important adsorption isotherm parameters, which are Henry's constant, maximum capacity, and diffusivity for CO_2 and CH_4 separation. However, their study was limited to carbon molecular sieve.
4. Gravimetric adsorption isotherm measurement for zeolite based material are very scarce.
5. Most of the measurement performed by chromatographic method follows Henry's isotherm while the measurement performed by other method follows Langmuir model.
6. 4A, 5A, 13X zeolite, and CMS have been claimed to be most suitable for CO_2/ CH_4 separation.

Based on the parametric studies, the following conclusions can be withdrawn:

1. Only Kapoor and Yang, (1989) have performed parametric analysis for CO_2/CH_4.
2. Most of the parametric studies analyze the process performance based on product purity and recovery.
3. Only the effect of pressure, composition, flow rate and temperature are the most important parameters that require optimization

CHAPTER 3
THEORY

3.1 Introduction

The operating condition of an adsorption separation depends on the adsorption mechanism. An understanding of the adsorption mechanism will provide some guidance for optimization the system. The three basic mechanisms of adsorption separation are equilibrium, kinetic, and steric. Almost all adsorption processes in the industry are based on equilibrium mechanism and only few are based on kinetic mechanism. Since steric mechanism is rarely utilized in industry, this work also will only concern on the equilibrium and kinetic mechanisms.

The equilibrium mechanism is based on the adsorption capacity difference of the adsorbent. The information regarding the adsorption capacity can be determined from the adsorption isotherm curve. Several models have been developed to predict the adsorption isotherm data. Among the favourite equations are Langmuir, Freundlich, Sips, Redlich and Peterson, Dubinin-Polanyi and Dubinin-Raduskhevich. These adsorption isotherms will be explained in the next section. These equations are not available in binary or multicomponent adsorption due to the occurrence of adsorption competition between the adsorbate. Langmuir and Sips proposed a multicomponent adsorption isotherm models, which give good prediction for multicomponent adsorption. The Langmuir and Sips multicomponent adsorption isotherm will be discussed in this chapter.

There are many methods to measure the adsorption isotherm. The comparisons of the various methods have been discussed in chapter 1. Despite its complexity, MSB gravimetric adsorption isotherm measurement method shows more accurate result compared to other method. The principle of MSB gravimetric measurement will be discussed in chapter 4.

In kinetic based mechanism, separation is based on the adsorption rate differences of the various adsorbates in the mixture onto the adsorbent surface. The adsorption rate is generally determined by mass transfer resistance (diffusion) compared to surface

adsorption itself. Based on the adsorbent pore size, there are two types of diffusion; macropore and micropore diffusion. Detail explanation of both types is given in this chapter.

Selectivity is the most important consideration for the selection of the best adsorbent for CO_2/ CH_4 separation. Selectivity can be divided into two types, kinetic selectivity and equilibrium selectivity. Nevertheless, capacity also plays an important role in adsorbent screening especially at high Henry's constant ratio. Detail explanation of selectivity and capacity for adsorbent screening will be discussed in the last part of this chapter.

3.2 Adsorption Type

Adsorption separation exploits the ability of certain solids to preferentially concentrate specific substance onto their surface. There are two distinguished adsorption types. The first type is physical adsorption or van der Waals adsorption. This type of adsorption is reversible and occurs as the result of van der Waals interaction between molecules of the solid and the adsorbed substance. When the intermolecular forces between solid and gas is greater than the interaction between molecules of the gas itself, the gas will condense upon the surface of the solid. The condensation process will be followed by a heat release. The adsorbed gas does not go through the crystal lattice of the adsorbent but remain upon the surface (Yang, 1987).

Another adsorption type is chemical adsorption, also called as activated adsorption. This type of adsorption occurs as the result of chemical interaction between the gas and the adsorbent. The heat liberated in this type is much higher compare to physical adsorption. The process is irreversible and the regeneration of the original substance will often be found to undergone chemical structure changes. Chemical adsorption is generally present in catalysis (Yang, 1987).

In industrial application, most of the adsorption separation is based on physical adsorption mechanism. Three distinguished physical adsorption mechanisms are steric, kinetic and equilibrium mechanisms. In steric mechanism, separation is performed due to the molecular sieving property of the adsorbent. In this case, big molecules are excluded and only small and properly shaped molecules can diffuse into the adsorbent. However,

in industrial applications, adsorption process based on steric mechanism is very rare. In kinetic mechanism, the separation by the kinetic mechanism is determined by diffusion rates difference among the adsorbate molecules to diffuse into the adsorbent. Most of the adsorption separation processes are based upon equilibrium mechanism. In equilibrium mechanism, the separation is achieved by capacity difference. Equilibrium and kinetic mechanism will be discussed in further detail in the following section (Yang, 1987).

3.3 Adsorption Equilibrium

In the equilibrium adsorption process, the adsorbent and the surrounding fluid reached equilibrium after sufficient contact time. In the corresponding state, the adsorbed amount is determined from the adsorption isotherm curve as shown in Figure 1.6. Adsorption isotherm can be described in many forms. Some of them are described by simplification of physical phenomena while others are purely empirical correlations. More number of the empirical parameters usually gives better fit to the experimental data. However, empirical equations do not have any practical significance since they can only be used for the range of variables where the parameters have been regressed. An overview of some single component and multi component adsorption isotherms will be given in the following sections.

3.3.1 Single Component Adsorption Isotherm

For single component system, Brunauer classified the adsorption isotherm into five different types as shown in Figure 3.1 (Ruthven et al., 1994). Many adsorption equilibrium models have been developed to predict these adsorption isotherms. At higher concentration, the adsorption isotherm becomes curved while at low concentration it becomes a straight line. In PSA system, the adsorption isotherm generally follows type I and II. For physical adsorption in microporous materials, such as zeolite and carbon molecular sieve, where the saturation limit depends on occupation of all surface sites, type I is commonly applied. A material such as activated alumina and silica gel generally shows type II behaviour. This isotherm type can be represented by BET equation. The

BET model is generally used to measure the surface area of adsorbent by adsorption of nitrogen at 77 K. The adsorption of hydrophobic material such as activated carbon is commonly represented by type III. This type corresponds to the situation where the sorbate-surface interaction is higher than the sorbate-sorbate interaction. The adsorption of macro or mesoporous material can be predicted accurately by type IV, while the adsorption of non porous material with high uniformity can be accurately predicted by type V.

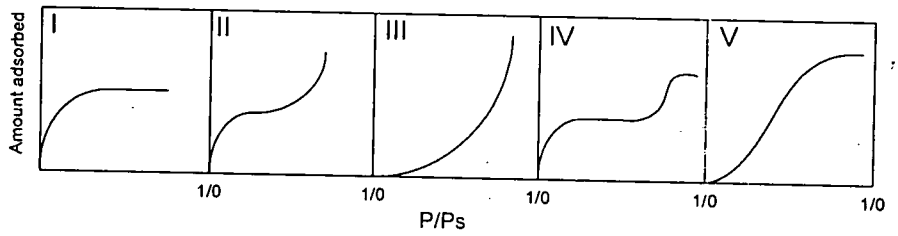


Figure 3.1 Brunauer adsorption isotherm classifications (Ruthven et al., 1994).

The adsorbed layer at the adsorbent surface may be regarded as a distinct thermodynamic phase. The equilibrium relationships generally approach a linear line at relatively low concentrations (Henry's law). All isotherms have to meet Henry's law at low concentration. Henry's law is a fundamental test for adsorption isotherm thermodynamic consistency. At low concentration, the adsorbed amount (q) is directly proportional with concentration (C) for liquid system or pressure (P) for gas system, and can be written as:

$$q = KP \text{ or } q = K'C \tag{3.1}$$

The proportionality constant (K or K') is referred as Henry's constant. The temperature dependence of this constant is shown in the following equation:

$$K' = K'o\, e^{-\Delta H/RT} \tag{3.2}$$

where ΔH and Ko' are the heat of adsorption and pre-eksponential factor respectively (Ruthven et al., 1994).

Based on dynamic equilibrium of the adsorption and desorption rates, Langmuir (1916) present theoretical adsorption isotherm model as written below.

$$\frac{q}{q_s} = \frac{bP}{1+bP} \tag{3.3}$$

where q_s is the maximum capacity and b is the equilibrium constant, which is directly related to Henry's constant by the following equation:

$$K=bq_s \tag{3.4}$$

Langmuir isotherm is classified as type I in Brunauer classification. Most of the gas adsorption applications usually fit this type of adsorption. The Langmuir model can often be used to represent the adsorption isotherm for microporous adsorbents. At low concentration the Langmuir equation will reduce to Henry's law (Ruthven et al, 1994).

Beside Langmuir isotherm, Freundlich (1926) proposed a simple empirical isotherm model as shown below:

$$q = bP^{1/n} \quad n>1 \tag{3.5}$$

Freundlich's model is based on the distribution of affinity among the surface adsorption sites, but it is probably better regarded as an empirical equation where b and n are empirical fitted constants that depend on temperature. Nevertheless, Freundlich isotherm does not reduce to Henry's law at low concentration. Therefore, this equation is thermodynamically inconsistent.

For better flexibility, Sips (1948) combine Langmuir and Freundlich equations to yield:

$$\frac{q}{q_s} = \frac{KP^{1/n}}{1+KP^{1/n}} \tag{3.6}$$

Unfortunately, this equation also does not confirmed with Henry's law at low concentration. Redlich and Peterson (1959) proposed another combined form as in the following equation:

$$\frac{q}{q_s} = \frac{aP}{1+bP^{1/n}} \tag{3.7}$$

This equation agrees with Langmuir equation at high pressure and with Henry's equation at low pressure (Mohd Shariff, 1995).

Langmuir and Freundlich are the most commonly observed isotherms for microporous adsorbent where monolayer adsorption is dominant. For multilayer adsorption, BET model is most suitable to predict multilayer adsorption which generally

utilized to predict adsorption isotherm for alumina and silica gel. The BET equation is written as:

$$\frac{q}{q_s} = \frac{b(P/P_s)}{(1-P/P_s)(1-P/P_s+bP/P_s)} \tag{3.8}$$

where P_s is the saturation vapour pressure.

All of the isotherms described above are based on surface adsorption. Polanyi (1932) derived adsorption isotherm based on pore filling model. In the pore filling model, it is assumed that adsorption takes place by attractive forces from the wall surrounding the micropores and the adsorbate molecules that start filling the pores volumetrically. In this approach, the adsorption equilibrium relation can be expressed in the form of adsorption potential (A) according to following equation:

$$W = q/\rho = f(A) \tag{3.9}$$

where W is the volume of micropore filled by the adsorbate, A is the adsorption potential and ρ is the density of adsorbed phase. The adsorption potential is defined as the work required to remove an adsorbate molecule from the adsorbed phase to the vapour phase and can be expressed as:

$$A = -RT\ ln(P/P_s) \tag{3.10}$$

The adsorbed amount as function of pressure can be determined by the correlation between the adsorption potential (A) and the volume of micropore filled by the adsorbate (W). The correlation is called the adsorption characteristic curve which was originally introduced by Polanyi (1914) and Berenyi (1920). Two of the best equations to determine the adsorption characteristic curve are Dubinin-Radushkevich and Dubinin-Astakov equations.

Dubinin-Radushkevich equation is derived by assuming a Gaussian distribution type for the characteristic curve. The equation is written as:

$$W = W_o\ exp\ (-kA^2) \tag{3.11}$$

This equation is then generalized by Dubinin and Astakhov into the following form;

$$W = W_o\ exp\ (-(A/E)^n) \tag{3.12}$$

where E is the characteristic energy of adsorption , k and n are the empirical constant (Suzuki,1990).

3.3.2 Multicomponent Adsorption

In adsorption of CO_2/CH_4 mixture, the adsorption isotherm becomes more complex since two or more adsorbates have the possibility to occupy the same adsorption sites. For binary mixtures at a given partial pressure, the quantity of mixtures adsorbed will be lower than single component system at the same partial pressure. A useful approximation like the single component Langmuir model is given by the following equation:

$$\frac{q_A}{q_{\max A}} = \frac{k_A P_A}{1 + k_A P_A + k_B P_B} \tag{3.13}$$

where k_A and k_B respectively are the Henry's constant for component A and B respectively, P_A and P_B respectively is partial pressure for component A and B respectively, and $q_{\max A}$ is maximum capacity of component A be adsorbed. Sips equation can also give good prediction for multicomponent system but the disadvantage of this equation is the empirical data that fit the equation have only little theoretical basis. The Sips equation for multicomponent system is given below.

$$\frac{q_A}{q_{\max A}} = \frac{k_A P_A^{1/nA}}{1 + k_A P_A^{1/nA} + k_B P_B^{1/nB}} \tag{3.14}$$

where n_A and n_B are empirical constants for component A and B respectively. Other multicomponent adsorption equation, such as Ideal Adsorbed Solution Theory (IAST), Vacancy Solution Theory (VST), and extended Dubinin-Radushkevich equation are also present. However, because of mathematical simplicity, extended Langmuir and Sips equation has been widely used for adsorption design (Ruthven, 1988).

3.4 Adsorption Kinetic

Most of the adsorption process is based on equilibrium separation, however, kinetic separation also plays an important role. Kinetic separation is based on the adsorption rate difference among the adsorbates. The most important kinetic separation in industrial

application is nitrogen production from air by using carbon molecular sieve. This method able to produce 99 % purity of nitrogen. The rate of physical adsorption is usually determined by the diffusion limitation rather than the surface adsorption itself. The diffusion mechanism depends on the mass transfer resistance from the adsorbent pore structure (Ruthven, 1988).

3.4.1 Adsorbent Pore Structure

Adsorbent can be divided into homogeneous and composite types based on pore structure type. In the homogeneous adsorbent, pore structure is similar through out the entire particle. Among the homogenous adsorbents are silica gel, activated carbon and activated alumina. On the other hand, the composite adsorbent is formed by aggregation of micropore in the particles. Commercial adsorbents in this class are peletted zeolites and carbon molecular sieve. The pore structure of the composite adsorbent consists of microporous voids in the crystals and intercrystaline macroporous voids within the pellet.

Composite adsorbent has three distinct mass transfer resistances that are macropore diffusion, micropore diffusion and external film. The illustration of these mass transfer resistances is shown in Figure 3.2. Microporous crystal has pore diameter smaller than 20Å (Ruthven, 1988).

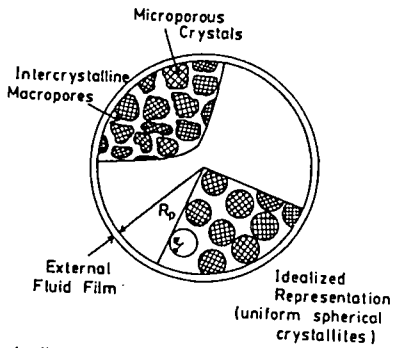


Figure 3.2 Mass transfer resistances (Ruthven, 1988).

Practically, the mass transfer in external fluid is very small, therefore the adsorption will be very rapid. The adsorption/desorption rate will be controlled by either micropore diffusion or macropore diffusion. (Ruthven et al., 1994).

3.4.2 Macropore Diffusion

There are four different diffusion mechanisms within a macropore which are bulk diffusion, Poiseuille diffusion, Waals diffusion, and surface diffusion. Bulk diffusion is the dominant mechanism where the pore diameter is larger than the mean free path. Mean free path is the average distance that an adsorbate can travel before being adsorbed (C.R. Nave, 2006). The bulk diffusion (D_m) can be calculated according to the following equation

$$D_m = 0.0018583 \frac{T^{1.7}}{P\sigma^2 \Omega \sqrt{M}} \tag{3.15}$$

where σ is the molecular diameter, Ω is the dimensionless function that can be found in Table B-2 of Bird et al. (1960) and M is the molecular weight (Do, 1998).

Knudsen diffusion (D_K) depends on the coalition between the pore wall and the diffusing adsorbate. It is significant at low pressure and in small pores where the mean free path is equal to or greater than the pore diameter. Knudsen diffusion is independent of pressure and only changes weakly with temperature. Knudsen diffusion is best described by the following relationship

$$D_K = \frac{2r}{3}\sqrt{\frac{8RT}{\pi M}} \tag{3.16}$$

where r is the pore diameter. Generally, both mechanisms are always occur together. The combined diffusivity (D_A) is described in the following equation.

$$\frac{1}{D_A} = \frac{1}{D_K} + \frac{1}{D_m} \tag{3.17}$$

There is also possible diffusion contribution from Poiseuille diffusion, which only significant at large pores and at high pressures. This diffusion is usually present in pressurisation step in PSA. The diffusion contribution is directly additive to the combined diffusivity from Bulk and Knudsen diffusion. The Poisuille diffusion (D_P) is given by the following equation

$$D_P = Pr^2/8\mu \tag{3.18}$$

where μ is the gas viscosity.

In the bulk, Knudsen, and Poiseuille diffusion, the adsorbates diffuse through the pore central region. In the case where the adsorbed phase is sufficiently mobile, there may be additional contribution from surface diffusion through the adsorbed layer on the pore wall. Any such contribution is directly additive to the previous combined diffusion. Surface diffusion is an activated process and in many ways similar to micropore diffusion, which will be discussed in the next section.

3.4.3 Micropore Diffusion.

Micropore diffusion occurs in the pores of dimensions comparable to the diameter of the diffusing molecules. In micropore diffusion, the diffusing molecule never escapes the adsorbent force field. In such small pores, it is difficult to differentiate between the adsorbed molecules and the gaseous molecule in the central of the pore. It is preferable that the entire gas molecules within the microparticle are considered as the adsorbed phase.

In the microporous adsorption process, the adsorbent surface concentration is time dependent. The adsorbent diffusivity is usually determined from the so-called uptake curve. Uptake curve contains information of the adsorbed amount as functions of time. The uptake curve is obtained by dividing the adsorbed amount at specific time (M_t) to the adsorbed amount at equilibrium (M_∞) and plot against time$^{0.5}$. The example of uptake curve is illustrated in Figure 3.3 (Kapoor and Yang, 1989; Keller and Staudt, 2005).

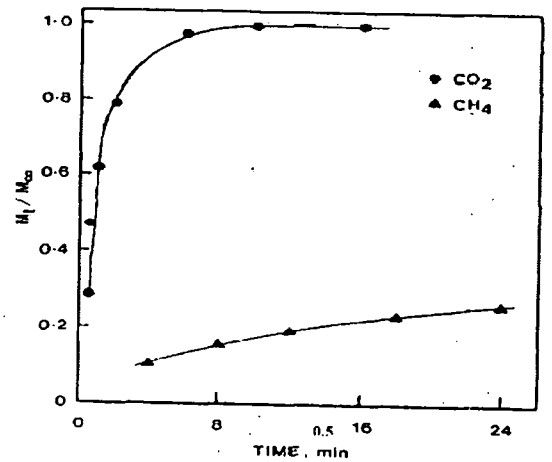


Figure 3.3 Typical uptake curve (Kapoor and Yang, 1989).

The diffusivity is calculated from the adsorbed amount as function of time M_t. The uptake curve is expressed in the following equation:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{e^{-n^2\pi^2 D_c t/r^2 c}}{n^2} \qquad (3.19)$$

where r_c, t, and D_c are microporous radius, time, and micopore diffusion respectively. There are two other simplified approaches to calculate the diffusivity. For fractional uptake <15%, the diffusivity can be calculated from the equation below:

$$\frac{M_t}{M_\infty} = \frac{6}{r^2 c}\sqrt{\frac{D_c t}{\pi}} \qquad (3.20)$$

For fractional uptake >70%, following equation will be used:

$$1 - \frac{M_t}{M_\infty} = \frac{6}{\pi^2}\exp\left(-\frac{\pi^2 D_c t}{r^2 c}\right) \qquad (3.21)$$

As an activated process, micropore diffusion (D_c) is strongly dependent on temperature and pressure. The dependence usually follows an Arrhenius form as shown in the equation below

$$D = D_\infty \frac{d\ln P}{d\ln q} e^{-E/RT} \qquad (3.22)$$

where E is diffusion activation energy and D_∞ is pre-exponential factor. The activation energy in small pore is higher than in larger pore adsorbent. The energy barrier is mainly due to repulsive interaction associated with molecule passing through the pore. Therefore, bigger molecular diameter will require higher activation energy.

3.5 Adsorbent Selection

For certain separation purposes, some adsorbents may be identified as suitable material. Preliminary selection can done using on the visual comparison of adsorption isotherm or uptake curve. However, visual inspection can be misleading sometimes and does not quantify the effectiveness of the separation. Two parameters are normally used to evaluate the effectiveness of the adsorption namely selectivity and capacity (Yang,

2002). Information regarding the capacity of the adsorbent can be obtained from the adsorption isotherm as discussed in the adsorption equilibrium section.

The selectivity of an adsorbent depends on its separation mechanism. The simplified selectivity in PSA is defined as follows:

$$\alpha = \frac{x_1}{x_2}\frac{y_2}{y_1} = \frac{q_1}{q_2}\frac{P_2}{P_1} \tag{3.23}$$

where α is the selectivity, x is the mole fraction of component 1 or 2 on adsorbent surface and y is the corresponding mole fraction in gaseous phase. Even though this parameter can be extended to other isotherm mode, it is preferable to use Langmuir isotherm model due to its simplicity and can give reasonable accuracy (Yang, 2002). By utilizing equation 3. 23, for Langmuir equation, this selectivity can be written as:

$$\alpha_E = \frac{K_1}{K_2} \tag{3.24}$$

where α_E and K are the equilibrium selectivity and Henry's law constant respectively.

For kinetic separation, the adsorption is performed only at short period to ensure the slower diffusion component does not have enough time to diffuse completely. For a short separation time the adsorbed amount will follow equation 3.20. For Langmuir adsorption isotherm, by substituting equation 3.3 in equation 3.20, the following equation is obtained:

$$q_t = \frac{KP}{1+bP}\frac{6}{r_c}\sqrt{\frac{D_1}{D_2}} \tag{3.25}$$

Habgood (1958) expressed the selectivity for kinetic separation as the product of Henry's constant ratio and the square root of the divusivity ratio. Thus, the kinetic separation factor is given by the equation below

$$\alpha_k = \frac{K_1}{K_2}\sqrt{\frac{D_1}{D_2}} \tag{3.26}$$

High selectivity adsorbent is usually selected as the main parameter to be considered for adsorbent selection. The selectivity can be inform of kinetic or equilibrium selectivity. However, under certain circumstances high capacity adsorbent is more important. For higher value of Henry's constant ratio, at the same partial pressure of adsorbate, the

contribution of weaker adsorbed component in the adsorption is small ($k_A P_A >> k_B P_B$). This situation can be observed from the equation below.

$$\frac{q_A}{q_{\max\ A}} = \frac{k_A P_A}{1 + k_A P_A + k_B P_B} \approx \frac{k_A P_A}{1 + k_A P_A} \tag{3.25}$$

$$\frac{q_B}{q_{\max\ B}} = \frac{k_B P_B}{1 + k_A P_A + k_B P_B} \approx 0 \tag{3.26}$$

It is very clear that at higher Henry's constant ratio the adsorption can be classified as single component adsorption and component B can be assumed as unadsorbed or inert. Unfortunately, to date, no single literature defines the Henry's constant ratio limit. Under this circumstance high capacity adsorbent is preferable.

CHAPTER 4
RESEARCH METHODOLOGY

4.1 Introduction

The research methodology consists of two major parts. The first part is the adsorption isotherm and kinetic measurements. The objective of the measurements is to select the best adsorbent for CO_2/CH_4 separation. Four potential adsorbent for CO_2/CH_4 separation were subjected to the measurement namely 4A zeolite, 5A zeolite, 13X zeolite, and carbon molecular sieve. The outcome of the measurements was data of mass of the adsorbed gas as function of pressure and time. This data can be further analyzed to calculate the equilibrium or kinetic selectivity and capacity which generally used as adsorbent screening criteria. In this work, the adsorption isotherm and kinetic measurements were performed using Magnetic Suspension Balance (MSB) which is based on gravimetric method.

The second part of this work is the dynamic studies of the best adsorbent selected from the first part. The main objective of the dynamic study is to observed the effect of regeneration temperature, feed composition, feed flow rate, and pressure on product (in this case CH_4) purity, recovery and productivity. The recovery and productivity were calculated based on the flow meter at the column outlet, while the purity of the product was analyzed using Gas Chromatograph (GC). The dynamic studies were carried out using Gas Adsorption Column Unit (GACU) developed in house. All the measurement for both parts were performed twice with deviation less than 5%. Example of the result reproducibility is given in appendix C.

All the adsorbent used in this experiment has 1 mm diameter. Carbon molecular sieve was supplied by Takeda Chemical Company, Japan while the zeolites were supplied by Zeochem, Switzerland. For adsorption isotherm measurement approximately 5 g of the adsorbent was required while for dynamic studies approximately 250 g of adsorbent was required. The porosity of 4A zeolite, 5A zeolite, 13X zeolite and carbon molecular sieve respectively are 0.71, 0.72, 0.72 and 0.23. The samples of the adsorbents used in this experiment are shown in Figure 4.1 to 4.4.

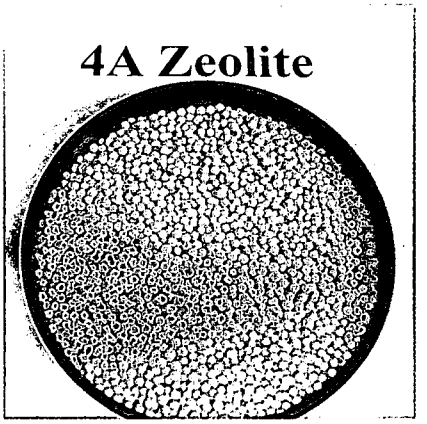


Figure 4.1 Sample of 4A zeolite.

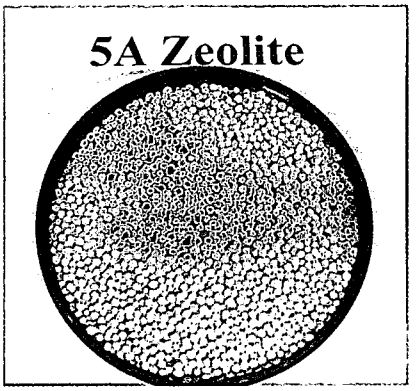
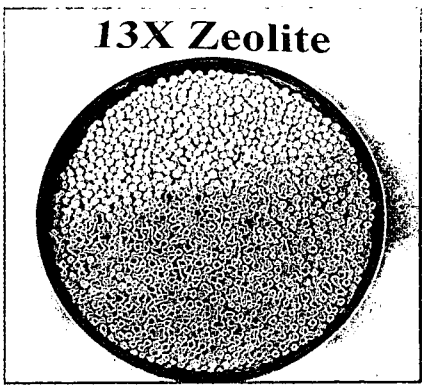
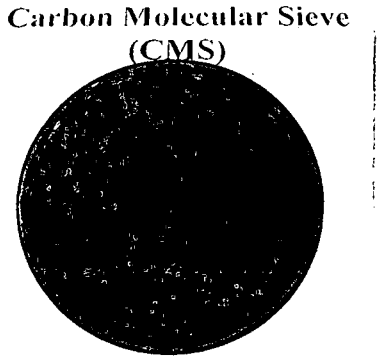


Figure 4.2 Sample of 5A zeolite.



4.3 Sample of 13X zeolite.



4.4 Sample of carbon molecular sieve (CMS).

4.2 Adsorption Isotherm and Kinetic Study

The adsorption isotherm and kinetic measurements are performed in order to determine the best adsorbent for CO_2/CH_4 separation. MSB gravimetric method is preferred for adsorption isotherm and kinetic measurements since it can produce accurate result, even though it is expensive and more complex. The adsorption isotherm and kinetic measurements are performed by using Rubotherm gravimetric adsorption isotherm unit. The unit consists of two major components, which are the Magnetic Suspension Balances (MSB) unit and the gas-dosing unit. The gas-dosing unit governs the amount and pressure of the gas in the system while the adsorption isotherm and kinetics are obtained from the magnetic suspension balance unit. Details on the Rubotherm gravimetric adsorption isotherm unit are given in appendix A. The schematic diagram and picture of Rubotherm gravimetric adsorption measurement unit are shown in Figure 4.5 and 4.6 below:

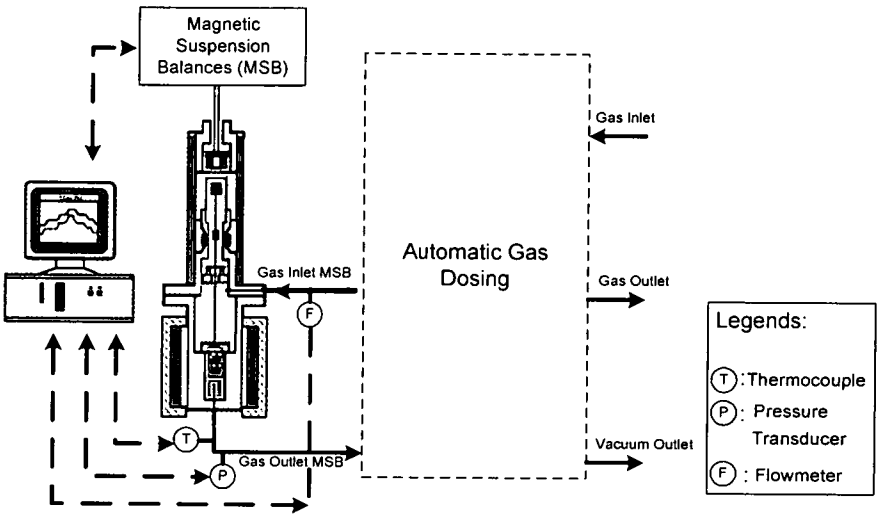


Figure 4.5 Schematic diagram of Rubotherm gravimetric adsorption measurement unit.

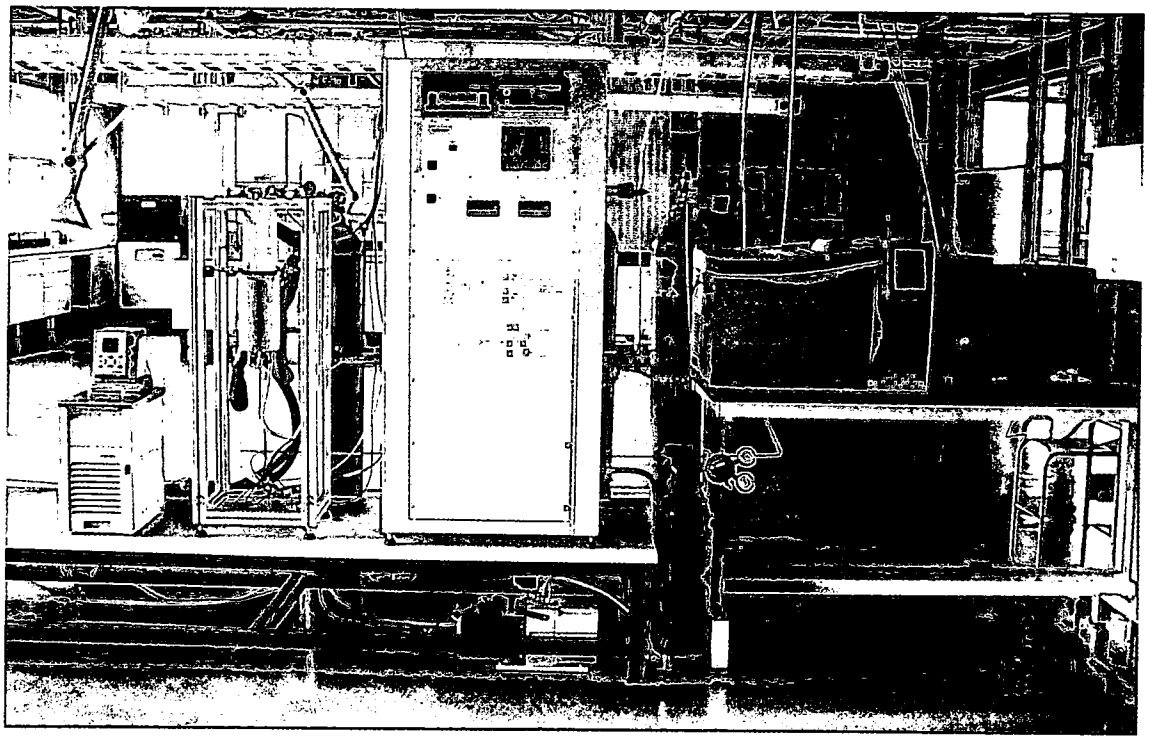


Figure 4.6 Rubotherm gravimetric adsorption measurement unit.

Rubotherm gravimetric measurement principle is based on the force balance between the weight of the system (F_A) and the buoyancy force (F_B). The weight of the system (F_A) is comprised of the weight of sample container, adsorbent, and adsorbate as given in the equation 4.1 below

$$F_A = (m_{SC}+m_S+m_A)g \qquad (4.1)$$

where m_{SC}, m_S, m_A, and g are mass of sample container, mass of adsorbent, mass of adsorbate, and gravity constant respectively. An illustration of the gravimetric measurement principle is given in Figure 4.7.

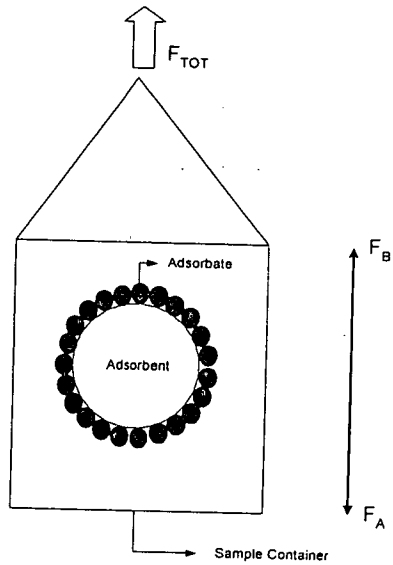


Figure 4.7 Illustration of principle of gravimetric measurements.

The buoyancy force (F_B) tends to lift the sample thus giving an opposite effect from the weight of the system. The principle of buoyancy effect is based on Archimedes law which can be expressed as in equation 4.2 below

$$F_B = (V_{SC}+V_S+V_A)\rho(T,P)\, g \qquad (4.2)$$

where V_{SC}, V_S, V_A, and ρ are volume of sample container, volume of adsorbent, volume of adsorbate, and gravity constant respectively.

The total force from MSB (F_{TOT}) can be easily calculated from the balances reading and can be expressed as in equation 4.3 below

$$F_{TOT} = m_{BAL}g = F_A - F_B = \{(m_{SC}+m_S+m_A) - (V_{SC}+V_S+V_A)\rho(T,P)\}\, g \qquad (4.3)$$

where m_{BAL} is the mass balances reading. Equation 4.3 can be simplified into equation 4.4 below

$$m_{BAL} = (m_{SC}+m_S+m_A) - (V_{SC}+V_S+V_A)\rho(T,P) \qquad (4.4)$$

The main objective of adsorption isotherm measurement is to measure the mass of adsorbate (m_A). Other parameters, such as the mass and volume of the sample and sample

container, can be determined from blank measurement and buoyancy measurement. Therefore, the MSB gravimetric measurement involves three procedures as follows:

a) Blank measurement
b) Buoyancy measurement
c) Adsorption isotherm and kinetic measurement

The principle of each step is given in the following section.

4.2.1 Blank Measurement

This measurement has to be performed only once after the installation of the equipment to determine the mass and volume of the sample container. This measurement is performed by measuring the mass of the empty sample container at different gas densities. It is preferable to use an inert gas such as helium or nitrogen for this measurement. In this work, nitrogen was used for the blank measurement.

The data required to determine the mass and volume of sample container are the weight of the balance (m_{BAL}) as function of pressure (P) and temperature (T) of the gas. Normally, this experiment is performed by using nitrogen, even though it is also possible to use other gas.

This measurement was performed by measuring the weight of the empty sample container at different gas densities. The density (ρ) of the gas can be calculated using equation of State (EOS) or measured directly from MSB. For ideal gas, the density of the gas can be calculated by the following equation:

$$\rho = \frac{MP}{RTZ} \tag{4.5}$$

where M, R, and Z are molar mass of the gas, ideal gas constant, and compressibility of the gas respectively.

By using titanium sinker, the density of the gas can also be calculated simultaneously with the adsorption measurement. The sinker is a hollow cylinder that has a known mass. By measuring the weight of the sinker at specific pressure, the mass of the gas inside the sinker can be calculated. The density of the gas can be calculated by following equation.

$$\rho = \frac{m_{gas}}{v_{gas}} \tag{4.6}$$

where ρ, m_{gas}, v_{gas} respectively are density of the gas, mass of the gas inside the sinker, and volume of the gas inside the sinker.

The experiment was performed by increasing the pressure stepwise from vacuum condition to a maximum of 60 bar with increment varying from 2 to 10 bar while keeping the temperature constant at 298K. At each pressure step, the weight of empty sample container measured by the balances was recorded and the gas density was calculated by equation 4.6. The weight of the empty sample container was then plotted against the density of gas as shown in Figure 4.8.

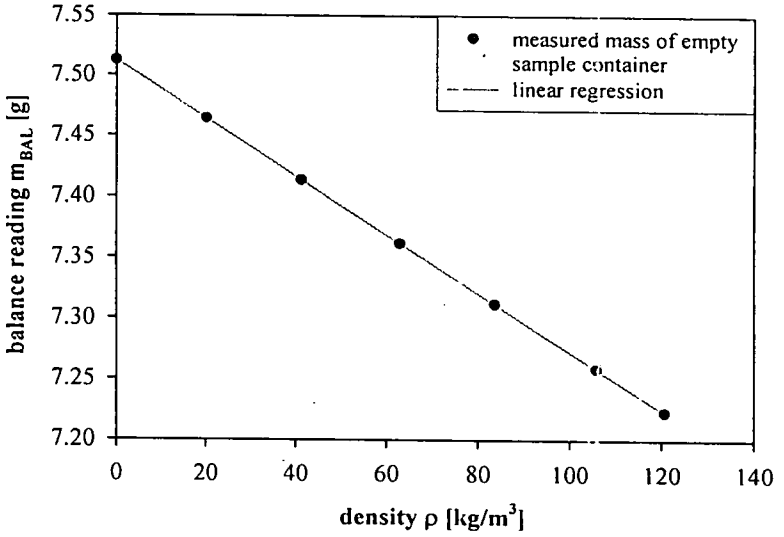


Figure 4.8 Typical result from blank measurement experiment.

The weight of the sample container recorded by the balances reduces as the pressure increases due to the buoyancy forces acting on the sample container. The buoyancy force (F_B) acts on any body which is located in a gas or liquid atmosphere and it is proportional with density (ρ) and volume of sample container (V_{SC}) of the body and also the gravity constant (g).

$$F_B = \rho V_{SC} g \tag{4.7}$$

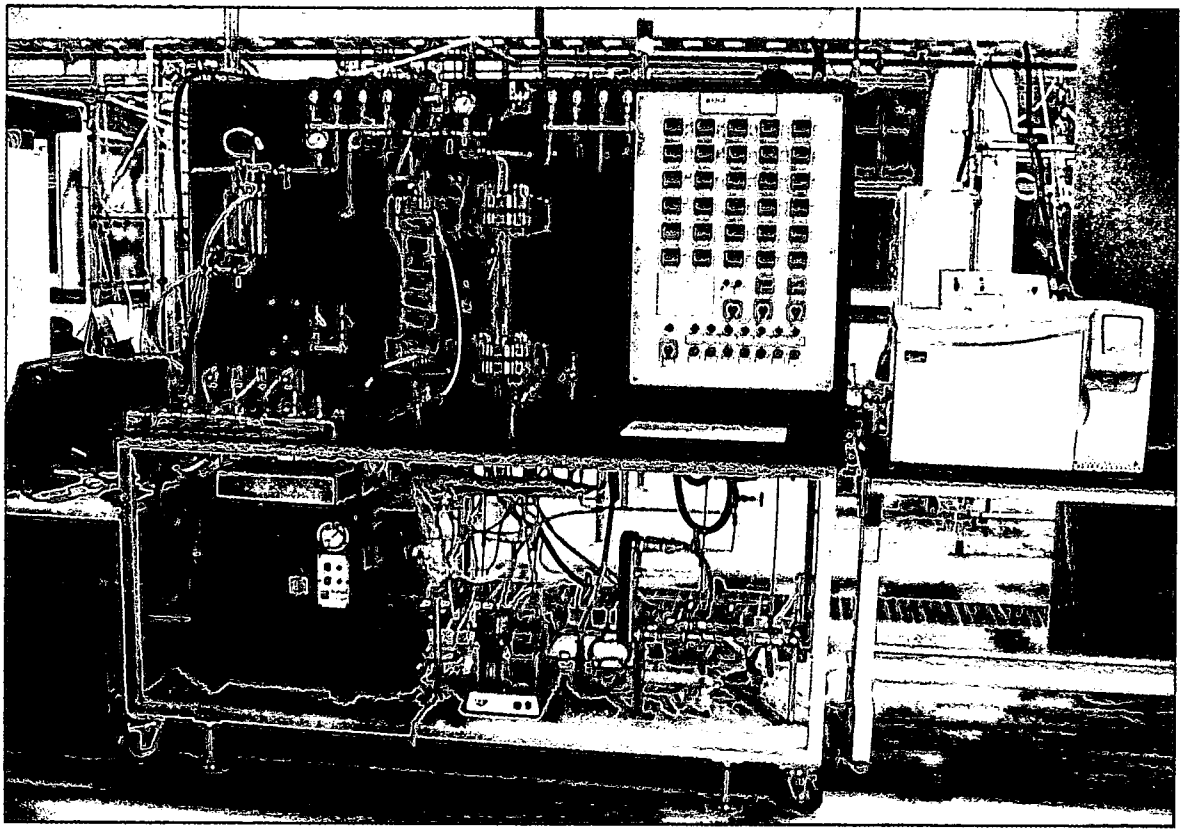


Figure 4.12 Gas Adsorption Column Unit (GACU)

4.3.1 Regeneration Temperature Variation Experiment

Prior to the regeneration experiment, the adsorption column was introduced with 50-50 mixture of CH_4/CO_2 mixtures at a rate of 2 NL/min until the adsorbent is saturated. The adsorbent is considered saturated when the outlet composition reaches 50% for both gases as indicated by the GC. The flow rate (2 NL/min) was selected since at higher flow rate the break through was very fast and it was difficult to observe from the GC. At lower flow rate the flow meter reading is less accurate because the accuracy of the flow meter is 1% of the maximum scale.

The selected composition 50-50 mixture of CH_4/CO_2 was selected since it was also used by other researchers such as Kapoor and Yang (1989) in their dynamic study. The adsorption bed was initially heated up to the desired temperature by the heating jacket and trace heater. The selected regenerant temperatures are 23, 50, 70, 100, 150°C. In this research air was chosen as the regenerant. After the bed has reached the set temperature,

5 NL of air was passed counter currently through the column to regenerate the column. Counter current regeneration cleans the adsorbent better compared to the cocurrent regeneration (Ruthven, 1988). The regeneration is considered completed when outlet flow rate is equal to the pure air flow rate.

To study the effect of temperature on adsorption performance, adsorption step was performed after the regeneration step. Once the bed temperature has cooled down to ambient temperature, 2 NL/min of 50-50 of CH_4/CO_2 mixture was introduced into the column. The adsorption step was stopped after the adsorbent was saturated ie. when the inlet and outlet composition were equal. From the hot gas regeneration experiment, it was determined that the best temp to regenerate the column is at ambient temperature. For subsequent dynamic studies, the column was regenerated at ambient temperature.

4.3.2 Composition Variation Experiment

Prior performing this experiment, the bed was regenerated by flowing 5 NL/min of air at ambient temperature through the column for about 30 minutes. This regeneration condition was selected according to the regeneration study which indicates that 29 minutes are required to regenerate the column at ambient temperature. After the column was completely regenerated, 5 NL/min mixture of CO_2/CH_4 was introduced to the column until the column saturated. The composition of the mixture was varied from 10% CO_2 until 90% CO_2 with 10% increment. The outlet flow rate of the column was continuously monitored from the outlet flow meter FI 06. The outlet flow rate information is required for recovery calculation.

The outlet gas was analyzed by GC for every two minutes. The GC reading is crucial for product purity information. After the column has reached saturation, the column was regenerated again in order to be used for the next adsorption experiment at different composition.

The total flow rate of 5 NL/min was selected since at different flow rate it is difficult to vary the composition. For example if the total flow rate at 7 NL/min is used, at 10% CO_2 composition, a flow rate of 0.7 NL/min of CO_2 and 6.3 NL/min of CH_4 will be required. Since the maximum flow rate of this flow meter is 5 NL/min therefore it is

impossible to obtain 6.3 NL/min of CH_4. On the other hand, at 3 NL/min the flow rate of CO_2 required is 0.3 NL/min and CH_4 is 2.7 NL/min. Since the accuracy of the flow meter is 1% full scale, therefore at 0.3 NL/min the error can be as big as 16.67%. Nevertheless, in this work, 3 and 7 NL/min total flow rate were also used for certain composition in order to study the effect of composition at different flow rate.

4.3.3 Flow Rate Variation Experiment

Similar to previous experiments, the column was regenerated first by flowing 5 NL/min of air at ambient temperature for about 30 minutes. This experiment was performed at ambient pressure and at 50-50 CO_2/CH_4 mixture. After the column has been completely regenerated, 1 NL/min of 50-50 mixture of CO_2/CH_4 was fed to the column until the column was saturated. The column outlet flow rate was monitored continuously by flow meter FI 07. The product purity was analyzed every two minutes by GC. After the column has reached saturation, another regeneration step was performed in order to clean the column for the next adsorption step at different flow rate. The flow rate was varied from 1 to 5 NL/min by adjusting the flow controller FI02 and FI03. Nevertheless, in this work, 30% and 70% NL/min composition were also used for certain flow rate in order to study the effect of flow rate at different composition.

4.3.4 Pressure Variation Experiment

The column was first prepared for this experiment by regenerating as in previous experiments. After the column has been completely regenerated, 50-50 of CO_2/CH_4 mixture at 2 NL/min was injected to the column at 2 bar pressure. At higher pressure, the column will reach saturation faster because large amount of gas enters the column. Therefore, in order to avoid rapid saturation of the column, the inlet flow rate was selected as low as possible. However, at 2 NL/min a longer time is required to pressurize the main column. Therefore, the second column was used to pressurize the main column by filling up the second column at double of the desired pressure. Once the pressure of the second column has reached double of the desired pressure, then the valve connecting

to the first column was opened. The gas flowed from the first column while the compressor was still compressing the gas until the pressure of the second column is reduced and equalize to the pressure in the first column as required. The system was then connected to the GC by opening valve V50. The outlet gas was sampled every two minutes and the composition was analyzed by an on-line GC. After the column was saturated, another regeneration step was performed in order to prepare the column for the next adsorption step at different pressure. The pressure was varied from 2 to 20 bar.

4.3.5. Recovery Calculation

The recovery of CH_4 can be calculated from the column outlet flow rate, which can be illustrated as in Figure 4.13 below.

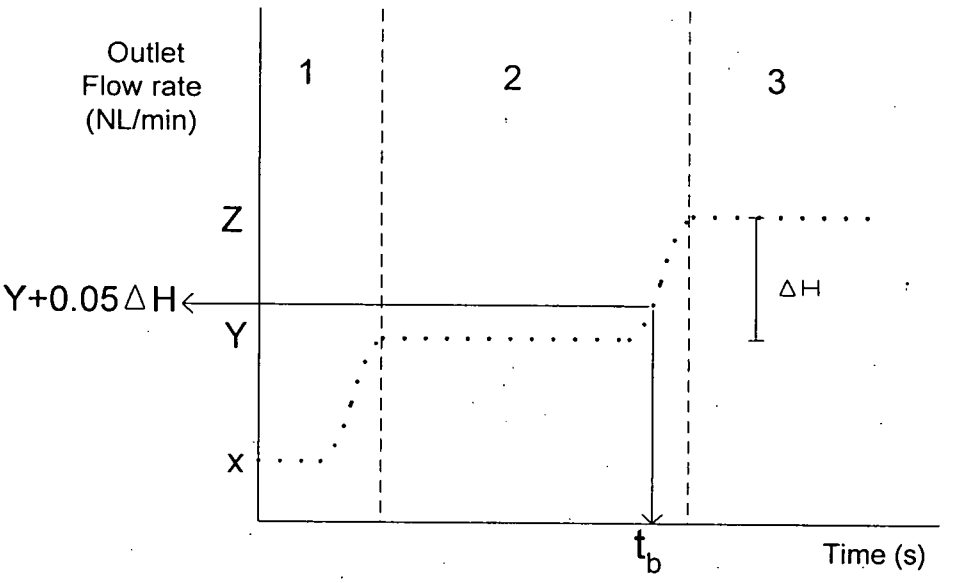


Figure 4.13 The pattern of column outlet flow rate.

Three distinct zones are present as shown in Figure 4.13. At Zone 1, both CO_2 and CH_4 are adsorbed and only a small amount of CH_4 passes through the column. At Zone 2, CH_4 has already completely passed through the column while CO_2 is still being adsorbed. In this zone, the real separation process happens since the entire CH_4 has passed through the column while CO_2 is still retarded. The CH_4 purity will be calculated from the GC reading in this zone. At zone 3, both gasses have already passed through the column and

the adsorption process has to be terminated. The variable X, Y, and Z and ΔH in the figure above is the flow rates of small amount of CH_4 which pass through the column, the flow rate of CH_4, the flow rate of CH_4 and CO_2, the flow rate of CO_2 respectively. In industrial applications, the adsorption process is terminated when the outlet flow rate contains 5% of CO_2 of inlet flow rate (Treyball, 1998). The time when the outlet flow rate contains 5% of CO_2 of inlet flow rate is called the break through time (t_b). This is the stopping criteria used in this work. In Figure 4.13 above, the breakthrough time is achieved at Y+0.05ΔH. The CH_4 recovery (%) can be calculated by equation 4.16 (Leuvenspiel, 1967).

$$Recovery\ (\%) = \frac{Mol\ of\ CH_4\ exit\ the\ column}{Mol\ CH_4\ enter\ the\ column} X\ 100\% \qquad (4.16)$$

For ideal gas, the molar ratio is equal to volume ratio. Therefore, equation 4.16 above can be replaced by equation 4.17 below.

$$Recovery\ (\%) = \frac{Volume\ of\ CH_4\ exit\ the\ column}{Volume\ CH_4\ enter\ the\ column} X\ 100\% \qquad (4.17)$$

Volume of CH_4 entering the column can be calculated by equation 4.18 below

$$Volume\ of\ CH_4\ enter\ the\ column = Y x\ t_b x CH_4\ Purity \qquad (4.18)$$

where Y and t_b are flow rate of CH_4 and break through time. Volume of CH_4 that exit the column is calculated based on the area under the curve as shown in Figure 4.14 below.

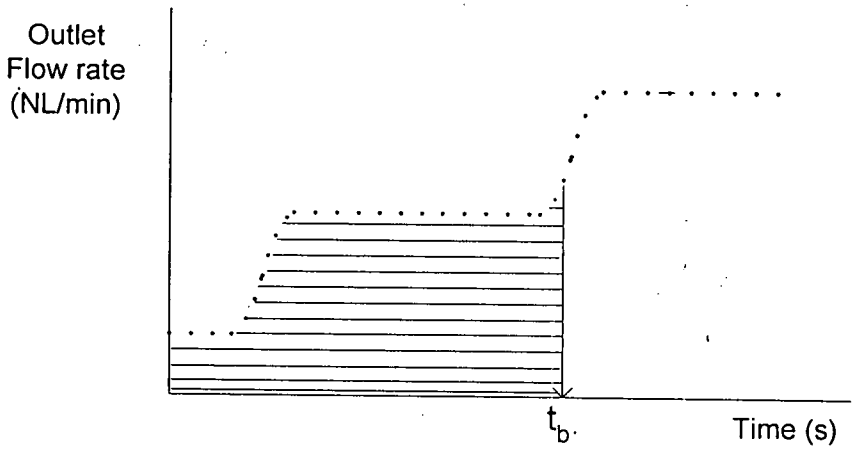


Figure 4.14 The pattern of column outlet flow rate for calculation of volume CH_4 exit the column.

The area under the curve can be calculated by Simpson's rule.

$$\text{Area} = \frac{F_i + 2F_{i+1} + 2F_{i+2} + 2F_{i+3} + \ldots + 2F_{n-1} + F_n}{2} n\Delta t \qquad (4.19)$$

where F_i is the data of flow rate number i, n is total data, Δt is the time between the flow rate data taken. In this work, the flow rate data was taken every second thus Δt equal to 1 second. Substituting equation 4.18 and 4.19 into equation 4.17, a new expression for recovery is obtained as given below.

$$Recovery\ (\%) = \frac{(F_i + 2F_{i+1} + 2F_{i+2} + 2F_{i+3} + \ldots + 2F_{n-1} + F_n)}{Y\ X\ t_b\ X\ CH_4\ Purity} n\ X\ 100\% \qquad (4.20)$$

4.3.6 Purity Calculation

The purity of CH_4 in the column outlet can be calculated by equation 4.21.

$$CH_4\ purity\ (\%) = 100\% - (\%\ CO_2) \qquad (4.21)$$

The percentage of CO_2 can be calculated from GC calibration curve at low product concentration is given in appendix D. From calibration curve, the % CO_2 is given by 7 $x10^{-5}$ (Area CO_2).Therefore, CH_4 purity can be calculated using the following equation:

$$CH_4\ purity\ (\%) = 100\% - (7.10^{-5}\ x\ Area\ CO_2) \qquad (4.22)$$

4.3.7 Productivity Calculation

The adsorbent productivity can be calculated by equation 4.23 (Waldron and Sircar, 2000).

$$Adsorbent\ Productivity = \frac{Volume\ of\ CH_4\ exit\ the\ column}{Total\ cycle\ time} \qquad (4.23)$$

CHAPTER 5
RESULTS AND DISCUSSIONS

5.1 Introduction

The results and discussion chapter is divided into three sections. The first section gives emphasis on the results from adsorption isotherm and kinetic experiments. The objectives of this section are to obtain and analyse Henry's constant, adsorbent capacity and diffusivity ratio which will be used for adsorbent screening. The second section covers the selection of the adsorbents for CO_2/CH_4 separation based on the adsorbent selectivity and capacity. Finally, the third focuses on the analysis of the effect of regeneration temperature, pressure, flow rate and composition to product (CH_4) purity, productivity, and recovery in the dynamic studies.

5.2 Adsorption Isotherm of CO_2 and CH_4

In the equilibrium-based adsorption studies, information obtained from the adsorption isotherms is very crucial for adsorbent selections. The adsorption isotherm for CO_2 and CH_4 on 4A, 5A, 13X zeolite and carbon molecular sieve (CMS) are shown in Figure 5.1 and 5.2 respectively.

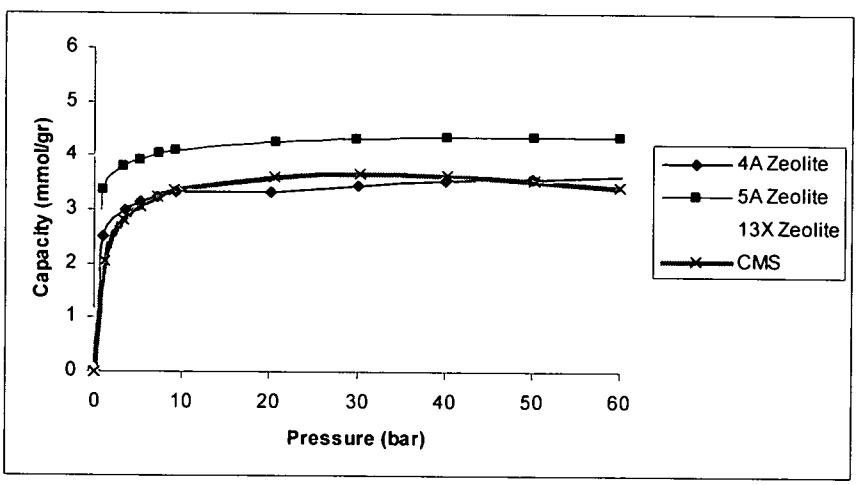


Figure 5.1 Adsorption isotherms of CO_2.

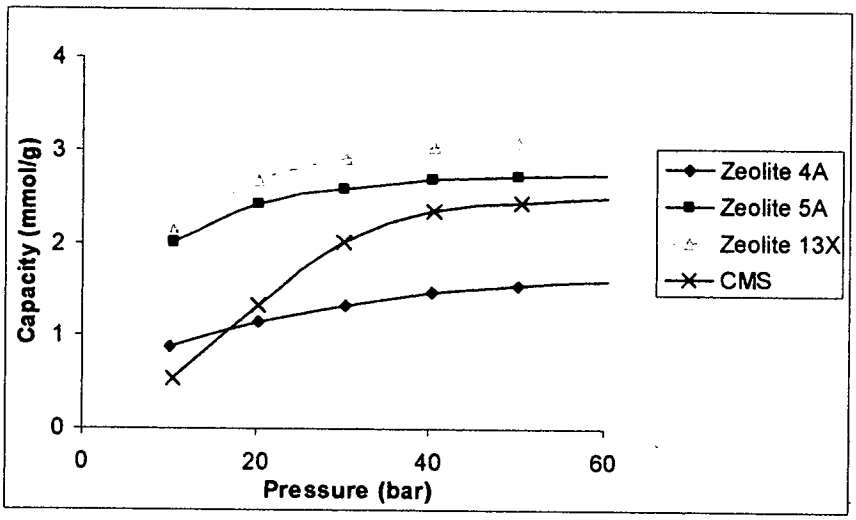


Figure 5.2 Adsorption isotherms of CH_4.

The results show that the adsorption isotherms for all adsorbents follow type 1 in Brunauer adsorption isotherm criteria (refer to Figure 3.1). For all adsorbents, the adsorption capacity of CO_2 is higher than CH_4. A comparison between all the adsorbents shows that 13X zeolite has the biggest capacity for both CO_2 and CH_4. The adsorbent capacity increases as the surface area of adsorbent increases. The data of the adsorbent surface area is given in Table 5.1 below.

Table 5.1 Adsorbent surface area.

NO	Adsorbent	Surface Area (m^2/g)
1	13 X zeolite	651
2	5A zeolite	528.35
3	4A zeolite	40.6
4	CMS	248

From the curves shown in Figure 5.1, it can be observed that the adsorption isotherm of CO_2 on CMS is decreasing slightly after the adsorption capacity reaches a maximum value.

Other researchers have also indicated that the adsorption capacity of CO_2 is higher than CH_4 in all the adsorbents that they have studied (Hernandez et al, 1997; Chaudary and Mahadevi, 1996; Harlick and Tezel, 2002; Nodzenki, 1998; Rolniak and Kobayashi, 1980; Pakseresh et al, 2002; Dexin and Youfan, 1987; Kapoor and Yang, 1989). However, the value of adsorption capacity obtained in this research is different with the

capacity observed from other research groups as given in Table 2.1 (Harlick et al. 2004; Rolniak and Kobayashi, 1980; Haq and Ruthven, 1985; Tezel and Apolonatos, 1992; Triebe and Tezel, 1996; Pakseresh et al. 2002; Kovach et al. 1998; Dexin and Youfan, 1987 and Kapoor and Yang, 1989). The difference is mainly due to different measurement method or different measurement conditions. To the best of author's knowledge, no other researchers have studied the adsorption of CO_2 and CH_4 on the selected adsorbents using magnetic suspension balances.

The adsorption capacity decreases at high pressure, especially for adsorption capacity of CO_2 on carbon molecular sieve. Other researchers also have similar observation for CO_2 adsorption on activated carbon (Herbs and Harting, 2002, Dreisbach et al, 2002, Keller and Staudt, 2005). The observation is more obvious at higher pressure since at higher pressure the buoyancy force acting on the adsorbate volume is no longer negligible (please refer to equation 4.3). The observation is also more obvious for CO_2 adsorption compare to CH_4 adsorption since the density of CO_2 is higher than CH_4.

There are two forces involved in physical adsorption namely van der Waals and electrostatic forces. Van der Waals force is always present in any adsorbent-adsorbate system while electro static force is only present in adsorbent which has an ionic structure such as zeolite. (Ruthven, 1988, Yang, 2002). The adsorption of CO_2 is higher than CH_4 for all adsorbents. This phenomenon can be explained from the forces involved in the physical adsorption. Zeolite adsorbents have highly polar surface that tends to attract polar molecules due to electro static force. Since CO_2 has higher polarity compared to CH_4, therefore CO_2 is more strongly adsorbed. In addition to the electro static force, on zeolite adsorbent, van der Waals force also contributes in the adsorption process. On the other hand, CMS has non-polar surface, therefore, the adsorption is controlled by van der Waals force only. The van der Waals force increases significantly as the adsorbate radius decreases. Since the diameter of CO_2 is smaller than CH_4 (3.3 Å and 3.8 Å respectively) therefore CO_2 is more strongly adsorbed on CMS compared to CH_4.

The higher adsorption of CO_2 than CH_4 in all of the adsorbents could also be due to the surface loading. The same adsorbent surface area can accommodate more CO_2, which is a smaller molecule than CH_4. Figure 5.3 give good illustration of this condition. The diameter of the white ball in Figure 5.3 is smaller than the black one. It can be observed

that the same area of square can accommodate more white balls than the black balls [Ruthven,1988].

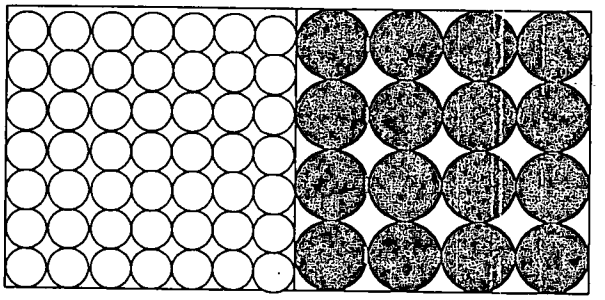


Figure 5.3 Adsorbate loading comparison on an adsorbent surface.

In comparison to CMS adsorbent, the adsorption force in zeolitic adsorbent is higher since the adsorption force in zeolite adsorbent not only involved with van der Waals force but also the electrostatic force. On zeolite, the electrostatic force increases as the number of exchangeable cation per cell increases. Both 4A and 5A zeolite have 12 exchangeable cation per cell while 13X zeolite has 10 exchangeable cation. Based on electrostatic force only, the adsorption force on 4A zeolite is stronger than the adsorption force on 13X zeolite. Nevertheless, from Figures 5.1 and 5.2, it is obvious that the adsorption capacity of CMS and 13X zeolite is higher than 4A zeolite. Therefore, it is confirmed that the capacity is not significantly affected by the adsorption force but mainly depends on the surface area of the adsorbent. From Figure 5.1 and 5.2 and Table 5.1, it can be observed that the adsorption capacity increases as the adsorbent surface area increases. This is due to higher surface area provide more space for the adsorbate to attach.

The adsorption isotherm curves in Figures 5.1 and 5.2 indicate type I in Brunauer adsorption isotherm criteria. This confirms that a microporous adsorption took place. In microporous adsorption, several correlations claimed to fit well with the first type of the adsorption isotherm. Among the popular equations suitable for microporous adsorbent are Langmuir, Freundlich, Sips, Redlich and Peterson, Dubinin- Radsushkevic and Dubinin-Astakhov (Ruthven, 1988; Ruthven et al, 1994; Yang, 1987; Mohd Shariff, 1995). Detail equations are given in Chapter 3. The parameters for these equations are regressed by using curve fitting tools in Matlab software and given in Tables 5.2 to 5.5 below.

Table 5.2 Langmuir adsorption isotherm parameters.

No	Adsorbent	Adsorbate	q_s	b	Accuracy (%)
1	4A Zeolite	CO_2	3.53	2.14	99.30
2	5A Zeolite	CO_2	4.31	3.11	99.53
3	13X Zeolite	CO_2	5.70	2.37	99.70
4	CMS	CO_2	3.66	1.11	99.37
5	4A Zeolite	CH_4	1.94	0.08	99.90
6	5A Zeolite	CH_4	2.99	0.20	99.88
7	13X Zeolite	CH_4	3.47	0.16	99.94
8	CMS	CH_4	5.07	0.02	96.95

Table 5.3 Freundlich adsorption isotherm parameters.

No	Adsorbent	Adsorbate	b	n	Accuracy (%)
1	4A Zeolite	CO_2	2.71	13.34	99.16
2	5A Zeolite	CO_2	3.53	17.57	99.61
3	13X Zeolite	CO_2	4.50	15.02	99.00
4	CMS	CO_2	2.50	9.93	95.25
5	4A Zeolite	CH_4	0.42	3.01	99.71
6	5A Zeolite	CH_4	1.43	6.01	99.57
7	13X Zeolite	CH_4	1.42	5.01	99.18
8	CMS	CH_4	0.19	1.53	95.03

Table 5.4 Sips adsorption isotherm parameters.

No	Adsorbent	Adsorbate	q_s	K	n	Accuracy (%)
1	4A Zeolite	CO_2	3.78	1.98	1.82	99.83
2	5A Zeolite	CO_2	4.61	2.70	2.08	99.99
3	13X Zeolite	CO_2	5.93	2.30	1.53	99.97
4	CMS	CO_2	3.67	1.12	1.01	99.22
5	4A Zeolite	CH_4	2.27	1.30	0.10	99.96
6	5A Zeolite	CH_4	2.90	0.14	0.84	99.99
7	13X Zeolite	CH_4	3.28	0.08	0.75	99.99
8	CMS	CH_4	2.72	0.001	0.43	99.77

Table 5.5 Redlich and Peterson adsorption isotherm parameters

No	Adsorbent	Adsorbate	q_s	a	K	n	Accuracy (%)
1	4A Zeolite	CO_2	3.81	3.45	4.24	1.04	99.86
2	5A Zeolite	CO_2	6.09	4.22	6.65	1.03	99.96
3	13X Zeolite	CO_2	4.12	4.27	3.67	1.03	99.94
4	CMS	CO_2	3.72	1.01	0.98	0.99	99.41
5	4A Zeolite	CH_4	3.42	0.12	0.60	1.31	99.87
6	5A Zeolite	CH_4	3.63	0.14	0.14	0.96	99.90
7	13X Zeolite	CH_4	3.74	0.11	0.08	0.92	100.00
8	CMS	CH_4	3.40	0.02	0.001	0.31	99.31

Dubinin-Radsushkevic and Dubinin-Astakhov equation parameters cannot be determined for this adsorption system since the calculation requires saturation vapour pressure of adsorbate at the temperature where the adsorption isotherm is developed. In this case, the adsorption isotherm was developed at 298K. Since the critical temperature of CH_4 is below 298 K, the saturation vapour pressure at 298 K does not exist.

From Tables 5.2 to 5.5 above, it can be observed that almost all of the equations can fit well with the experimental adsorption isotherms with the accuracy greater than 99%, except for CMS where the accuracy is greater than 95%. From Figure 5.1, it can be observed that CMS capacity for CH_4 adsorption is higher than 13X zeolite. Nevertheless, it is noticed from Figure 5.1 that the CMS is only achieved 50% of its maximum capacity (2.5 mmol/g) at 60 bar. This low capacity increment explains the reason why the Henry's constant for CH_4 adsorption on CMS is very low. Due to its high capacity, CMS can be potentially used for CH_4 storage. However, this property is not useful for CO_2/CH_4 separation since high CH_4 capacity can reduce the adsorbent selectivity.

For selectivity calculation, due to its accuracy, Langmuir equation is preferred by many researchers (Ruthven, 1988; Yang, 2002; Ruthven et al., 1994). Selectivity calculation, as given by equation 3.24, requires information regarding Henry's constant value (K). The K value can be determined from the slope of the adsorption isotherm curve as the pressure approaches to zero. At this pressure, Langmuir equation becomes:

$$\lim_{P \to 0} q = \frac{q_{\max} bP}{1 + bP} = q_{\max} bP \tag{5.1}$$

The Henry's constant (K) can be obtained from the product of q_{max} multiplied by b. The Henry's constant and the maximum capacity (q_{max}) of all the adsorbent are shown in Table 5.6 below. These parameters will be used to determine the most suitable adsorbent for CO_2/CH_4 separation. The selection of adsorbent is discussed in the following section.

Table 5.6 Henry's constant and maximum capacity.

Adsorbent	K_{CO_2}	K_{CH_4}	$q_{\max CO_2}$	$q_{\max CH_4}$
4A	8.04	0.16	3.55	1.89
5A	15.08	0.60	4.26	3.00
13X	14.58	0.53	5.69	3.50
CMS	4.16	0.09	3.65	5.47

5.3 Adsorption Kinetic Measurement

In kinetic based adsorption, the adsorbent screening is done based on the diffusivity ratio, which can be calculated from the uptake curve. The uptake curves provides the information regarding the fractional uptake ($\frac{m_t}{m_\sim}$) as function of time. The fractional uptake itself is a fraction of the time-dependent adsorbed amount (m_t) fraction to the adsorbed amount at equilibrium ($m_\sim$). The uptake curves for this experiment are shown in Figures 5.4 to 5.7.

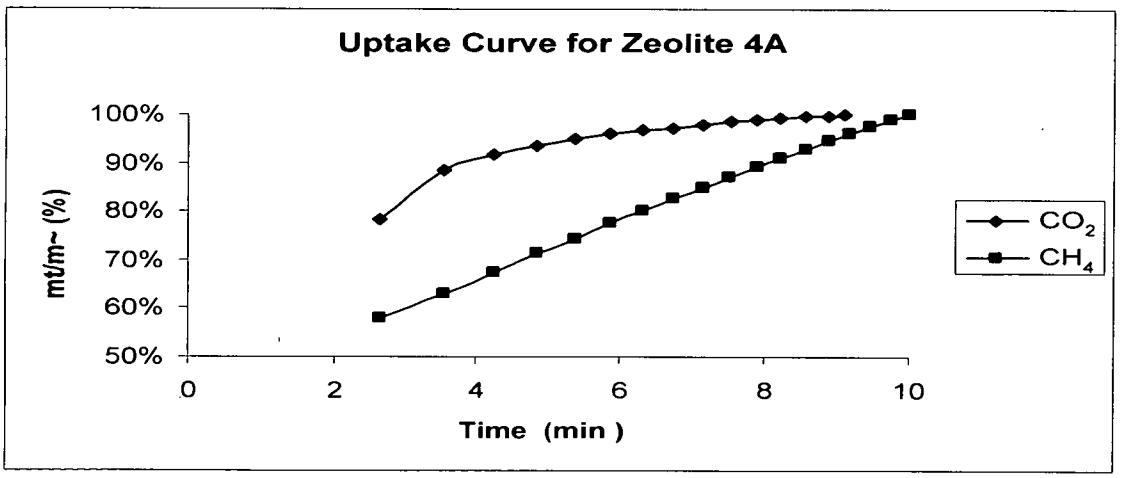


Figure 5.4 Uptake curve for 4A zeolite.

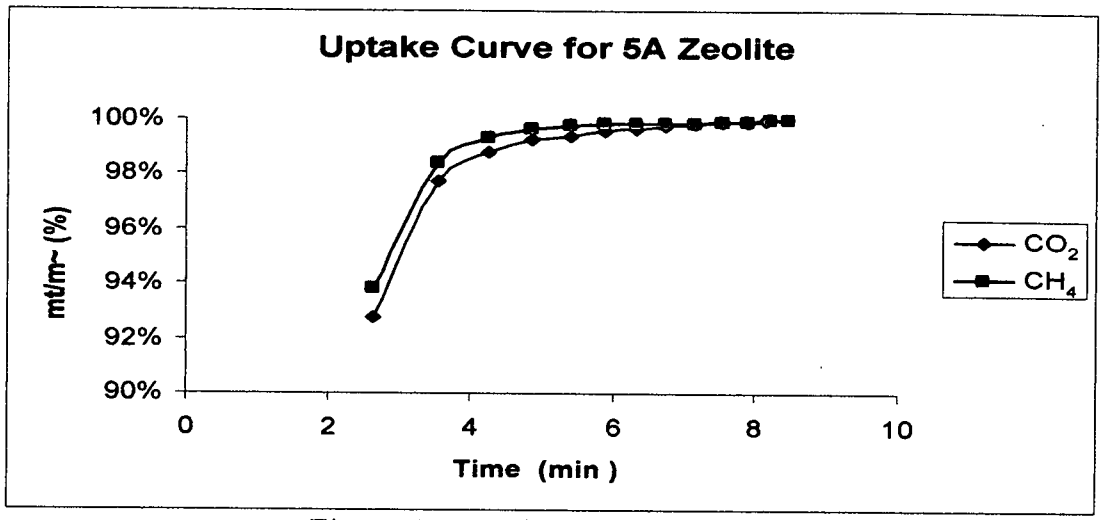


Figure 5.5 Uptake curve for 5A zeolite.

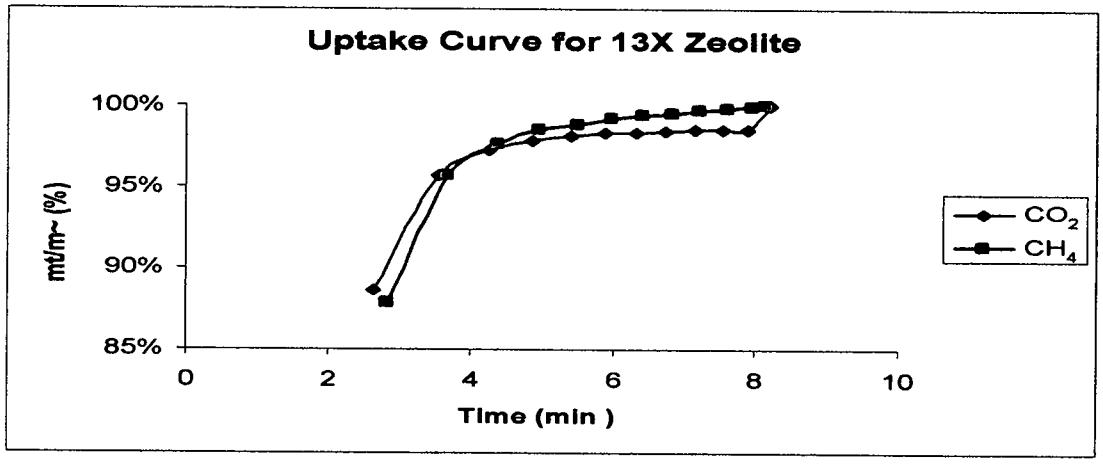


Figure 5.6 Uptake curve for 13X zeolite.

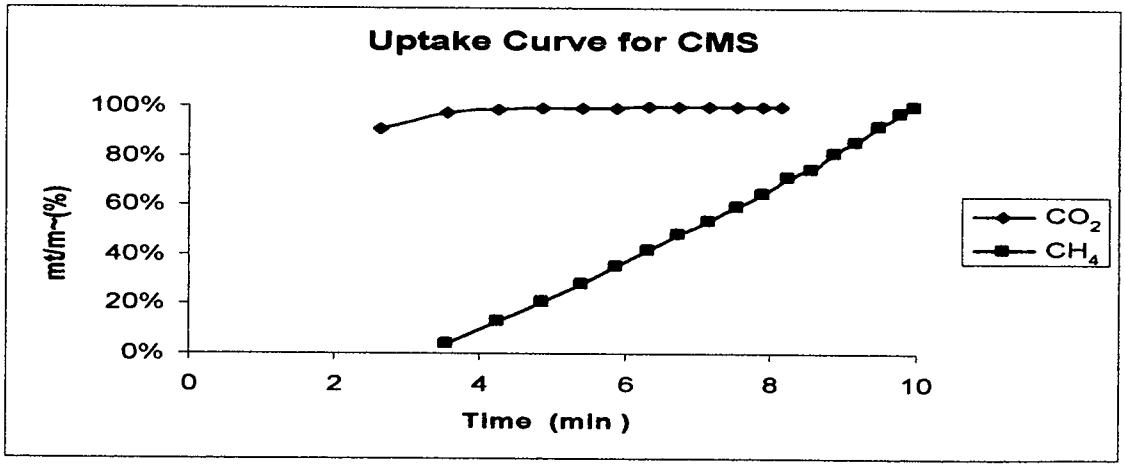


Figure 5.7 Uptake curve for CMS.

From the uptake curves, it is found that all the adsorbents adsorbed CO_2 rapidly. For 5A and 13X Zeolite, both CO_2 and CH_4 are adsorbed quickly thus the uptake curves

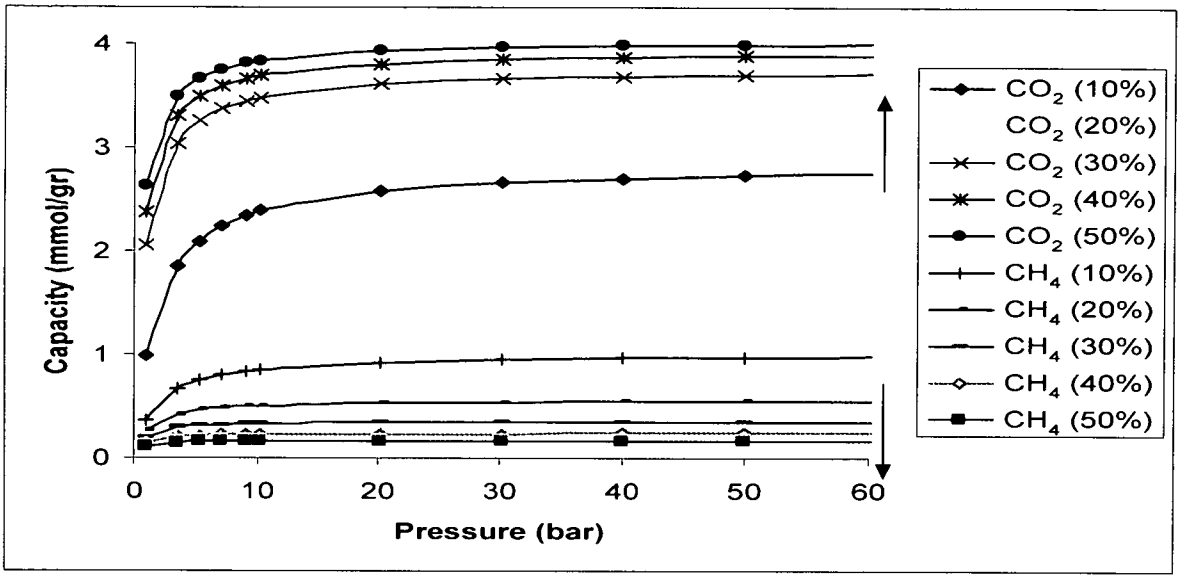


Figure 5.9 Binary adsorption isotherm curve for 5A zeolite.

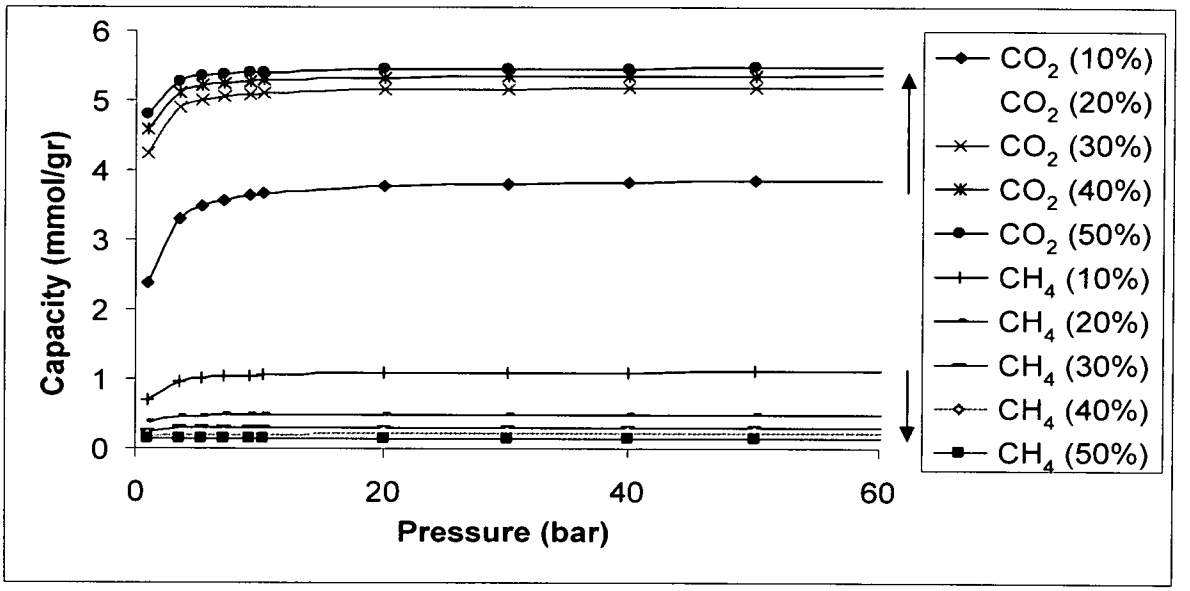


Figure 5.10 Binary adsorption isotherm curves for 13X zeolite.

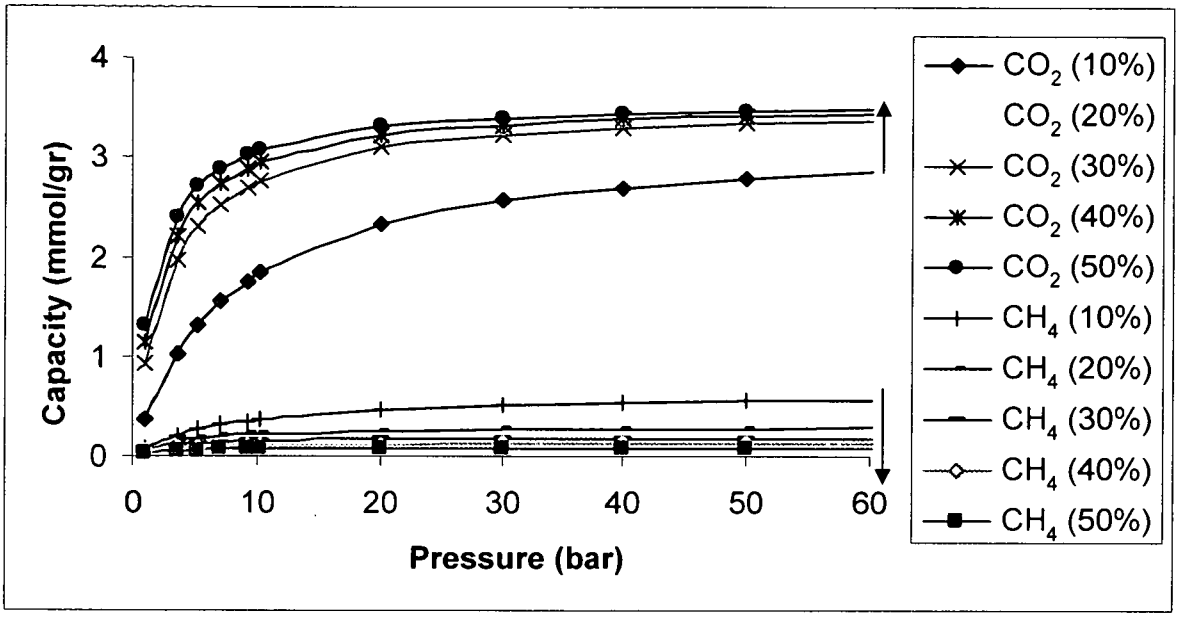


Figure 5.11 Binary adsorption isotherm curve for CMS.

The binary Langmuir adsorption isotherm shows that at higher CO_2 composition the adsorption capacity of CH_4 is reduced and the value approaches zero. This is due to lower Henry's constant of CH_4 than the Henry's constant of CO_2, as given in Table 5.6. Since CH_4 capacity approaches zero at very high CO_2 concentration, therefore it is no longer required to emphasis on the selectivity for bulk separation. During bulk separation, CO_2 adsorption capacity is more important than equilibrium selectivity.

Among those adsorbents, CMS shows the best selectivity with selectivity value of 379.07. Despite its large selectivity factor, the adsorption capacity of CMS is smaller than 13X zeolite as given in Table 5.8. Therefore CMS is only suitable for purification purposes. For bulk separation of CO_2/CH_4, high capacity adsorbent is more important. Zeolite 13X is used for the dynamic adsorption studies since it has the highest CO_2 adsorption capacity.

5.5 Dynamic Adsorption Study

The main purpose of the dynamic study is to the study the effect of regeneration temperature, feed composition, feed flow rate, and pressure to the performance of the system. Except for regeneration temperature study, the performance of the system is

evaluated based upon product purity and recovery. For regeneration temperature effect study, the performance of the system is evaluated based on adsorbent productivity. Detail explanation and calculation regarding recovery, purity and productivity is given in chapter 4. Result and discussions of the dynamic studies will be discussed in the following sections.

5.5.1 Effect of Regeneration Temperature

Some adsorbents require high temperature regeneration condition which consumes higher energy and requires a longer cooling down period. Consequently, these conditions causes additional cost for energy requirement and reduce the productivity of the bed. In this regeneration study, the effect of regeneration temperature to productivity is also observed. The result of the experiment is shown in Table 5.9 below.

Table 5.9 The effect of regeneration temperature to productivity.

No	Regeneration Temperature (^{o}C)	Time to Reach Temperature (min)	Cool Down Time (hr)	Regeneration Time (min)	Adsorption Time (s)	Total Time (hr)	Productivity (LCH_4/kghr)
1	25	0	0	29	476	0.62	139.08
2	50	15	2.5	27	478	3.65	23.56
3	75	23	4	20	475	9.1	9.39
4	100	30	6	12	482	9.52	9.11
5	150	41	8	12	490	10.49	8.4

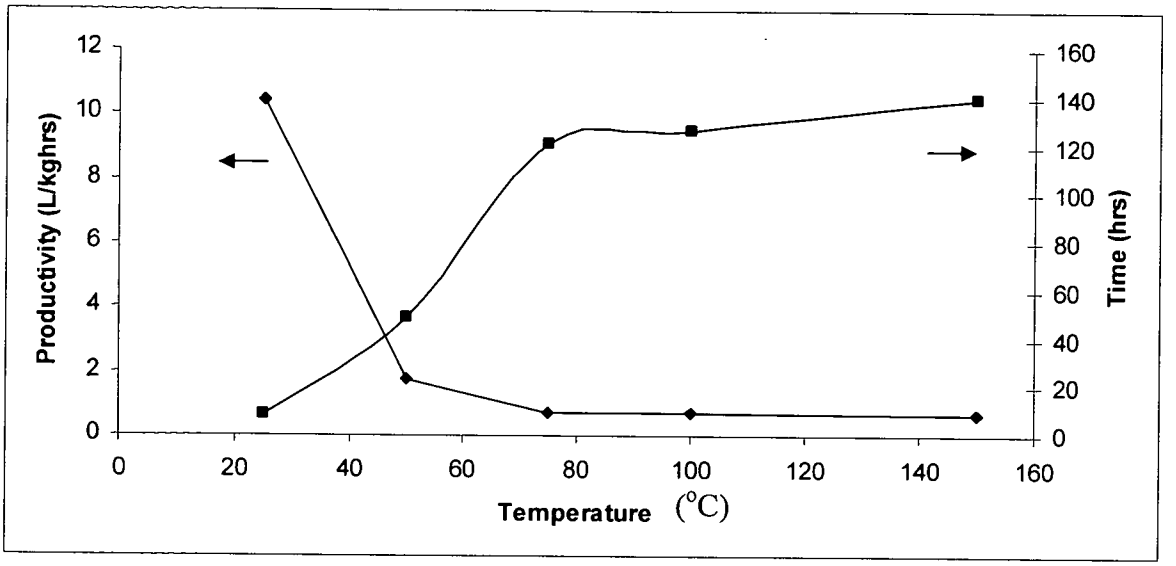


Figure 5.12 The effect of regeneration temperature to productivity.

It can be observed that at higher temperature, the total regeneration time of the column is also longer. A major portion of the total regeneration time is the time to cool down the column. Since adsorption is an exothermic process, high temperature can reduce the capacity of the column. Therefore, the column has to be cooled down first before conducting the next adsorption step. The higher the regeneration temperature, the longer the cooling down time, thus reduces the productivity of the adsorbent. However, at high temperature the column can be regenerated quickly.

The productivity of the column decreases rapidly as the temperature increases. It is observed that at ambient temperature the productivity of the column is higher than at other temperature. The productivity was calculated as the product (CH_4) obtained per cycle time per kg adsorbent [Waldron and Sircar, 2000]. After each regeneration step, an adsorption test was performed in order to check the purity of the product as a result of the previous regeneration. The purity of the product remains constant at 99.8 % for all regeneration temperatures. The adsorption time for all regeneration temperature is similar. This indicates that the adsorption capacity is not significantly affected by the regeneration temperature.

The results obtained from these experiments are significantly different from the research by Talu et al. (1996) which was focused on air separation of using 5A zeolite. Their result indicated that a change in regeneration temperature ($\pm 20^{\circ}C$) will increase the adsorbent capacity by 25%. On the other hand, Huang and Fair (1989) in their studies on the effect of temperature studies in adsorption of ethane and propane mixture using activated carbon found a similar trend with the result obtained from this work. At higher regeneration temperature, the regeneration time is faster but a longer time is required to cool down the column.

The results of the experiments indicate that the adsorption of CO_2 is best when the column was regenerated by ambient gas stripping only. The productivity of the adsorbent at ambient temperature is better compared to higher temperature since the cooling down is not required. Column insulation is important to maintain column temperature and prevent heat loss but it has the opposite effect for cooling process.

In these experiments, the regeneration step was terminated when the outlet flow rate was equal to the pure air inlet flow rate which is 5 NL/min. At the initial step of the regeneration, the outlet flow rate was higher than the pure air inlet flow rate since the air is also carry the adsorbate. The column is considered clean from the adsorbate when the air flow rate is reduced to the pure air flow rate (Huang and Fair, 1989).

5.5.2. Effect of Composition

The composition variation study in this work was only performed for high CO_2 concentration feed only. The dynamic adsorption apparatus used in this research is only sensitive for measurement up to 10%. It is not accurate enough to be used for purification purposes, which requires accuracy more than 95%. The CO_2 composition in the feed used in this study was varied from 10 to 90%.

The accuracy of the flow meter used in this experiment is 1% of full scale. At 1 NL/min, an error of 10% is introduced into the flow meter reading. Generally, the statistical acceptance criterion for the error introduced by measurement is only 5% (Montgomery, 2005). If the total flow rate exceeded 7 NL/min, it would be difficult to analyze the CH_4 purity since the breakthrough time would be tremendously fast, while

the GC requires minimum of two minutes perform the analysis. In this work a suitable flow rate that compromised between measurement error and ease of purity analysis need to be determined. It was found that at 4-6 NL/min the measurement can be performed with good accuracy and the product purity can still be analyzed. Finally a flow rate of 5 NL/min was determined as the most suitable flow rate with reasonable error of measurement. The flow rate was adjusted by setting the percentage of valve opening at the flow controller. Since the flow meter of each gas has 5 NL/min flow rate at maximum opening, thus the composition of the feed is similar to the percentage of valve opening. The experimental result of the variation composition is shown in Table 5.10.

Table 5.10 The result of variation of composition,

No	Flowrate (NL/min)	CO_2 Composition (%)	Recovery (%)	Purity (%)
1	5	10	93.75	99.72
2		20	92.08	99.89
3		30	91.55	99.89
4		40	88.68	99.89
5		50	85.28	99.9
6		70	81.52	*
7		90	64.84	*
8	3	30	94.16	99.86
9		40	92.34	99.73
10		50	90.16	99.81
11		60	87.11	99.71
12		70	82.95	99.48
13	7	30	90.37	99.33
14		40	89.82	98.92
15		50	88.08	*
16		60	85.36	*
17		70	82.00	*

* : The CH_4 purity cannot be analyzed due to fast breakthrough of GC

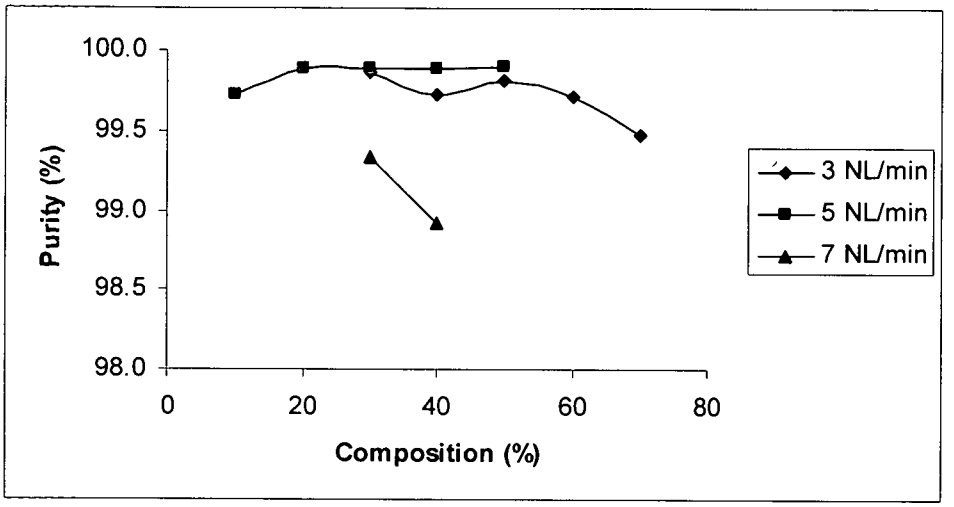


Figure 5.13 The result of variation of composition to product purity

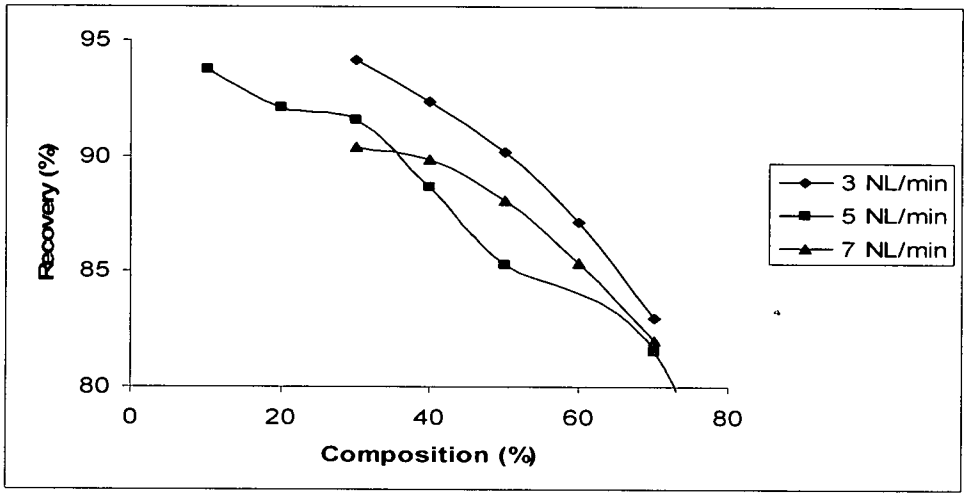


Figure 5.14 The results of variation of composition to product recovery

The results indicate that variation of composition. The variation of composition does not affect product purity but affect the recovery. The recovery of CH_4 is reduced at high CO_2 composition. However, the findings of Waldron and Sircar (2000) and Diaggne et al. (1995) show that the product purity decreases as the amount of strongly adsorbed component amount increases. However, their studies were performed on different separation system. Waldron and Sircar studied the separation of CH_4 and H_2 while Diagne et al. studied the separation of N_2 and O_2 in air. On the other hand, the study on recovery shows good agreement with the results from Dong (1998), Waldron and Sircar (2000) and Diaggne et al. (1995). Even though none of them studied similar adsorption

systems but the some trend of tend decreasing recovery with increasing amount of strongly adsorbed component were also observed.

The reason for the constant purity is not well understood. There is a high possibility that this is due to fast diffusivity of CO_2 on 13X zeolite. At high diffusivity, there is a small possibility that small portion of the CO_2 can pass through the column unadsorbed via the void. However, this hypothesis has not been proven.

At higher CO_2 composition, the amount of adsorbed CH_4 is reduced because the adsorbent site that used to adsorb CH_4 is now occupied by CO_2. Therefore, the capacity of 13X zeolite to adsorb CO_2 is increase. This finding is confirmed with the binary Langmuir adsorption shown in Figure 5.10. The reduction of CH_4 capacity on 13X zeolite, at high CO_2 composition, leads to early breakthrough on the adsorption. Since recovery is calculated based on CH_4 produced at the CO_2 breakthrough time therefore early breakthrough will lead to recovery reduction.

5.5.3 Effect of Flow Rate

Flow rate selection is very important not only for equilibrium-based adsorption but also for kinetic-based adsorption. For equilibrium based separation, proper selection of flow rate is vital to ensure sufficient time for the adsorption to occur. For kinetic based adsorption, flow rate will determine the selectivity of the adsorbent. In this study, 50% CO_2 and 50% CH_4 was used.

Table 5.11 The results of variation of flow rate.

No	CO_2 Composition (%)	Flowrate (NL/min)	Recovery (%)	Purity (%)
1	30	3	94.16	99.86
2		4	93.58	99.69
3		6	92.40	99.40
4		7	90.37	99.33
5	50	2	87.36	99.84
6		4	88.17	99.90
7		6	88.99	99.75
8		8	87.27	*
9		10	89.75	*

No	CO_2 Composition (%)	Flowrate (NL/min)	Recovery (%)	Purity (%)
10	70	3	82.95	99.48
11		4	82.42	99.67
12		6	83.44	*
13		7	82.00	*

* : The CH_4 purity cannot be analyzed due to fast breakthrough of GC

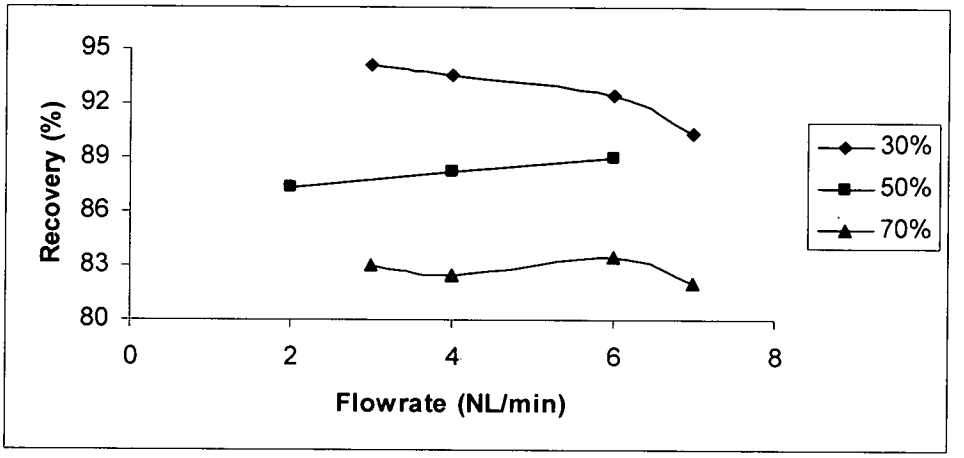


Figure 5.15 The results of variation of flow rate to recovery.

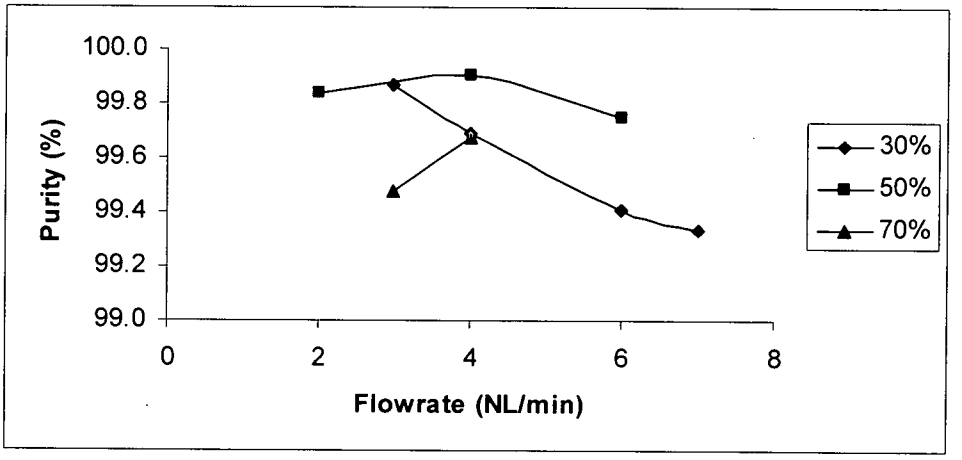


Figure 5.16 The results of variation of flow rate to purity.

No specific pattern of recovery as function of flow rate was observed. However the purity of the product seems to be unaffected by flow rate since a similar purity was observed at all flow rate and CO_2 composition at approximately 99.5 % purity. The findings of this experiment differs from the results of Mendes et al. (2001) and Gomes and Yee, (2002). Their studies showed that the product purity decreases and recovery increases as the product flow rate increases. However, their studies were not for the

separation CO_2/CH_4 on 13X zeolite. Mendes et al. (2001) studied air separation by 5A zeolite while Gomes and Yee (2002) studied the separation of CO_2 in flue gas by 13X zeolite.

At higher flow rate, the residence time of the feed gas in the column was reduced thus there was only short time available for the adsorbent to adsorb the gas. At total flow rate of 8 NL/min, the product purity cannot be analyzed by GC. The GC requires 2 minutes to analyse the gas composition whereby the adsorbent was already saturated at less than 2 minutes.

5.5.4 Effect of Pressure

It is preferable to perform adsorption at high pressure since at high pressure more gas can be adsorbed and higher product purity can be obtained. However, at high pressure, adsorption of valuable component also increased thus reducing the recovery. This experiment was performed using a 50-50 of CO_2/CH_4 mixture. This composition was selected since in most cases the composition of CO_2 in natural gas is lower than 50%. If good separation can be achieved at 50-50 of CO_2/CH_4 mixture, the system will also give good separation for lower CO_2 concentration. In order to reduce early breakthrough the gas flow rate was selected as minimum as possible. Therefore, in this experiment 1 NL/min flow rate was chosen for each gas. The experiment was also conducted at 2 NL/min flow rate but the breakthrough was very fast thus no result can be obtained. The result of the study is given in Table 5.12 below.

Table 5.12 The results of pressure variation experiment.

No	Pressure (bar)	Recovery (%)	Purity (%)
1	2.2	93.92	99.92
2	3.8	86.55	99.92
3	7.3	72.32	99.90

* : The CH_4 purity or recovery cannot be analyzed due to fast breakthrough of GC

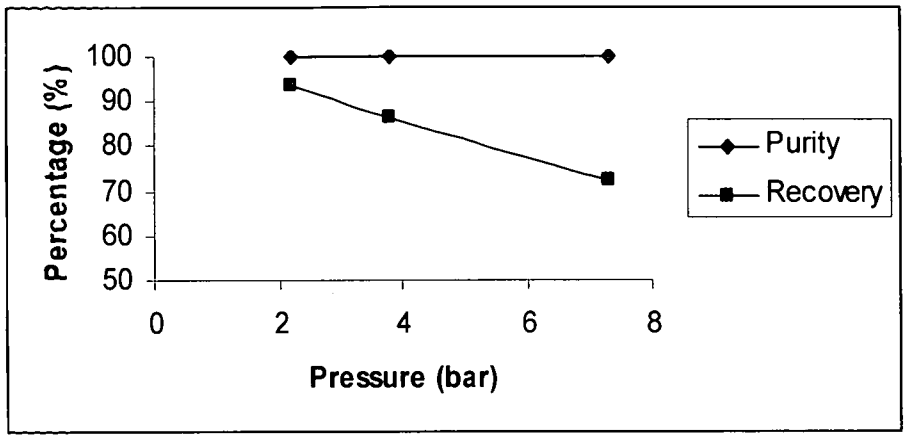


Figure 5.17 Pressure variation effect on purity and recovery.

From Table 5.12, it can be observed that purity nearly remained unaffected for the whole range of the experiments. The experimental results are in good agreement with Huang and Fair (1989). The purity of methane in the product remains constant for the whole range of experiment. The purity trend differs from the findings by Yang (1989), Ruthven et al. (1994), Waldron and Sircar (2000), Warmuzinski and Sodzawiczny (1999), Gomez and Yee (2002), and Chuo and Chen (2004). The main reason why the purity remains constant for the whole pressure range is due to fast diffusivity of CO_2 on 13X zeolite. At high diffusivity, it is imposible for any amount of CO_2 can pass through the column unadsorbed. At higher pressure the diffusivity of the gas is faster thus ensure almost all the CO_2 adsorbed in the adsorbent. However, at pressure higher than 7.3 bar, recovery and purity can not be predicted since the breakthrough was very fast.

At high pressure the amount of CH_4 adsorbed also increases therefore recovery decreases. This observation is in good agreement with Huang and Fair (1989) at low pressure region. However, as the pressure increased they found that recovery becomes constant and not affected by pressure. In this experiment the constant recovery region was not detected because of rapid saturation of the adsorbent at high pressure.

CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

From the experimental result obtain in this work several general conclusions can be drawn as follows:

1. 13X zeolite is the most suitable adsorbent for bulk separation of CO_2 while CMS is more suitable for natural gas purification from CO_2.
2. The regeneration of CO_2 is best performed by ambient temperature gas stripping Only since high temperature will reduce productivity.
3. Lower CO_2 composition in the feed mixture can increase CH_4 recovery without significant effect on purity.
4. Flow rate changes does not significantly affect purity and recovery.
5. No significant result was observed for pressure variation study due to rapid breakthrough.

6.1.1 Adsorption Isotherm of CO_2 and CH_4

Adsorption isotherm and kinetic measurement were performed in order to select the best adsorbent for CO_2/ CH_4 separation. The equilibrium and kinetic parameters of four potential adsorbents for CO_2/ CH_4 separation, which are 4A zeolite, 5A zeolite, 13X zeolite, and carbon molecular sieve were evaluated and compared. The selection criteria were mainly based on adsorbent capacity and selectivity.

The adsorption isotherm data show that the adsorption capacity of CO_2 is always higher than CH_4 for all adsorbents. This is because CO_2 has smaller molecular size compared to CH_4. Smaller molecular size gives stronger van der Waals force. Further more, at the same adsorbent surface area, more gases of smaller molecule size can be accommodated compared to bigger molecule size.

The larger the surface area, more CO_2 and CH_4 can be adsorbed. This is because of higher surface area provides more space for the adsorbate to attach. The order of the adsorbents based on the surface area from larger to smaller is 13X zeolite> 5A zeolite>

CMS> 4A zeolite. However, the adsorbent surface area not the only parameter that determine adsorption capacity. Electrostatic forces also plays an important role to influence the adsorption capacity value. Even though CMS has higher surface area compare to 4A zeolite but 4A zeolite has higher CO_2 capacity due to the influence of electrostatic force. The result indicated that 13X zeolite has the highest capacity for both CO_2 and CH_4 adsorption.

All of the adsorption isotherm curves indicate a type I in Brunauer adsorption isotherm criteria thus confirming that microporous adsorption occurs. The experimental adsorption isotherms can fit well with well-known adsorption isotherm models for microporous adsorbent such as Langmuir, Freundlich, Sips, Redlich and Peterson with the accuracy greater than 99%, except for CMS where the accuracy is greater than 95%.

The diffusivity of the gas increases as the adsorbent pore size increases or the adsorbate molecular size decreases. The molecular size of CO_2 is smaller than the pore size of all the adsorbent thus promoting fast mass transfer of CO_2 to the adsorbent active sites. On the other hand, the adsorption of CH_4 on 4A zeolite and CMS requires longer time since the pore size is approximately the same as CH_4 molecular size. For 5A and 13X Zeolites, both CO_2 and CH_4 are adsorbed quickly thus the uptake curves almost overlap each other.

The adsorption selectivity is calculated based on Henry's law constant and diffusivity ratio which can be determined from adsorption isotherm and uptake curve. The selectivity calculation indicate that CMS has higher selectivity compared to other adsorbents, which are more suitable for removal of CO_2 from natural gas. The selectivity of CMS adsorbent is based on kinetic selectivity.

For the separation of CO_2/CH_4 mixtures, binary adsorption isotherm is used since both CO_2 and CH_4 components are simultaneously adsorbed. The binary Langmuir adsorption isotherm shows that at higher CO_2 composition the adsorption capacity of CH_4 is reduced and the value approaches zero. This is due lower Henry's constant of the CH_4 than the Henry's constant of CO_2. Since the CH_4 capacity is reduced to zero at high CO_2 concentration, therefore the adsorption capacity of CO_2 in the mixture is depends solely on the single component capacity of CO_2. In this case, for bulk separation of CO_2, it is more important to select adsorbent that gives high CO_2 capacity rather than high

selectivity. Therefore, 13X zeolite has been selected for the dynamic adsorption studies since it has the higher CO_2 capacity among the selected adsorbents.

6.1.2 Dynamic Adsorption Study

Parametric study was performed in order to study the effect of operating parameters on product purity, recovery and productivity for CO_2/ CH_4 separation using dynamic adsorption unit. The operating parameters that were investigated were regeneration temperature, composition, flow rate and pressure. The performance of the system was analyzed based on the product purity, productivity and recovery.

The adsorption purity of the adsorbents is not significantly affected by the regeneration temperature. At higher regeneration temperature, a longer time is required to achieve the desired temperature and to cool down the column, thus reduce the productivity of the adsorbent. However, at high temperature the column can be regenerated quickly. The results of the experiments indicate that the regeneration of CO_2 is best performed by ambient temperature gas stripping only.

The composition variation study indicates recovery was affected while purity was not affected by variation of composition. The recovery of the gas is reduced at high CO_2 composition. The results show that 13X zeolite can still be used to separate CO_2 from natural gas stream even at 70% CO_2 with product purity of 99.48% but with low recovery of 82.95%.

There is no specific pattern of recovery as function of flow rate. The purity of the adsorbate is unaffected with the value of more than 99% regardless the flow rate used. Therefore, the adsorption system still can produce good separation for the whole flow rate used in this experiment. The maximum flow rate used in this experiment is 10 NL/min per 200 gram of adsorbent.

The purity of the product remains constant for the whole pressure range considered in this experiment (i.e 1-7 bar). The pressure variation study indicates that as the pressure increases the recovery of the gas decreases. At pressure higher than 7 bar the column was saturated rapidly due to the small size of the column. Therefore it was not possible to calculate the product purity and recovery.

It is not well understood why purity was unaffected for the whole operating conditions used in this study. There is a possibility that this is due to fast diffusivity of CO_2 on 13X zeolite. At fast diffusivity, it is impossible for any amount of CO_2 to pass through the column unadsorbed.

6.2 Recommendations

6.2.1 Adsorption Isotherm of CO_2 and CH_4

In this work only CH_4 was used to represent natural gas for this adsorption study. It is recommended to use real natural gas composition to observe the effect of other component on natural gas on the adsorption process.

The binary adsorption isotherm used in this study was predicted based on the binary Langmuir adsorption isotherm equation. It would be better if the prediction can be confirmed by actual adsorption isotherm measurement for binary mixture.

6.2.2 Dynamic Adsorption Study

The current experimental studies are limited to regeneration temperature, composition, flow rate, and pressure. It is recommended that other parameters should also be considered such as purge gas pressure, evacuation pressure, and feed to reflux ratio. Other than product purity and recovery it is also recommended to evaluate the system performance by considering thermal and mechanical strength of the adsorbent as well.

The current parametric studies for pressure variation are limited to less than 7 bar to avoid rapid saturation of the adsorbent. It is suggested that bigger columns or lower range of mass controller to be used.

A more vigorous studies should also be considered by developing adsorption and regeneration model for scale up purpose.

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APPENDIX A
RUBOTHERM MSB GRAVIMETRIC ADSORPTION UNIT

The Rubotherm MSB gravimetric adsorption unit consists of two major components, which are Magnetic Suspension Balances (MSB) unit and the gas-dosing unit. The schematic apparatus for Rubotherm MSB gravimetric adsorption measurement unit is shown in Figure A.1 below:

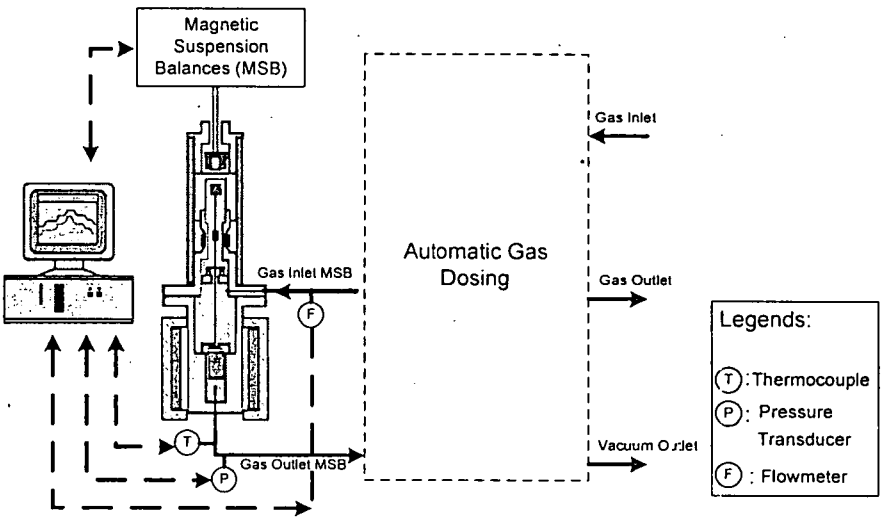


Figure A.1 Rubotherm MSB gravimetric adsorption measurement unit.

The gas-dosing unit governs the amount and pressure of the gas in the system while the adsorption isotherm and kinetics are obtained from the magnetic suspension balance unit. The pressure of the system depends on the outlet pressure of the gas cylinder only without additional compressor. The temperature of the system is controlled by an electrical jacket heater and internal heat exchanger. The external electrical jacket heater can be heated up the system up to 450°C. For temperature below 150°C, the system is heated up by heat transfer medium through internal heat exchanger. The temperature of heat transfer medium is controlled and pumped by JULABO oil bath thermostat. The output signals obtained from the apparatus are transmitted to a PC, which automatically controls the equipment.

Gas dosing unit allows the system to perform measurement either in static or flowing condition with the pressure up to 150 bar. Detail of the gas dosing unit compartment is given in Figure A.2.

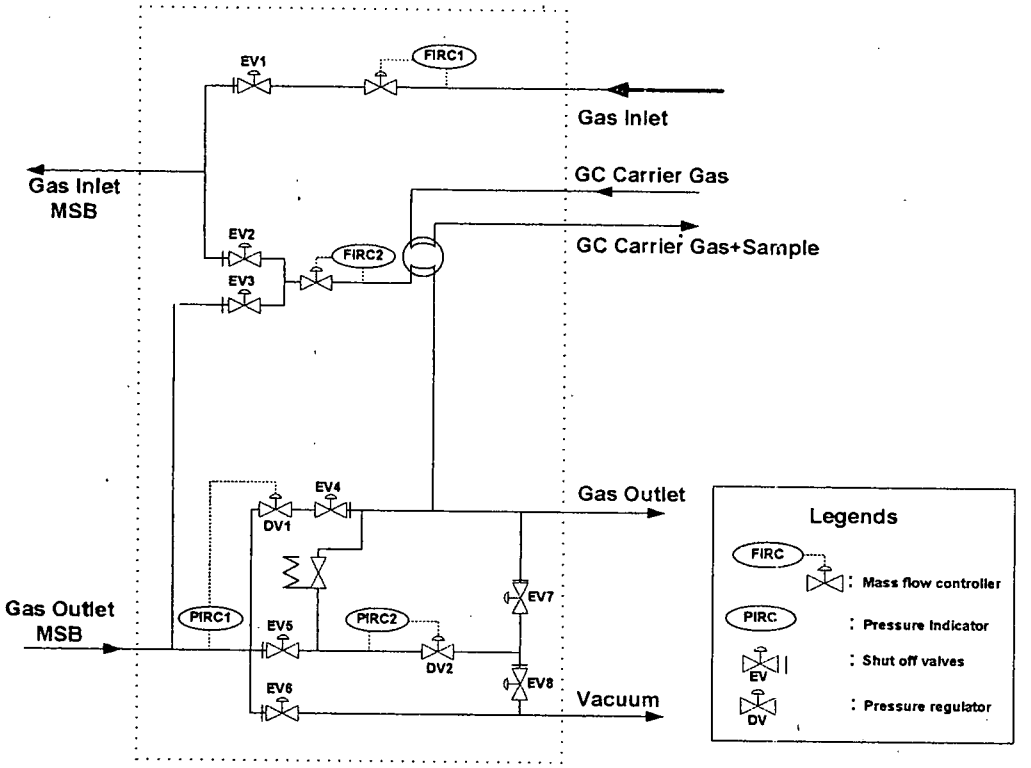


Figure A.2 Gas-dosing unit.

The flow of the gas is directed by eight electromagnetic shut off valves (EV1-EV8) according to user setting. The amount of gas injected is governed by Bronchorst mass flow controller (FIRC-1) model F-231 M-FAA-33-Z. The measurement range of FIRC-1 is from 0 to 0.5 NL/min with 1% reading scale accuracy. The gas dosing unit can also be used for multicomponent adsorption isotherm measurement by combining this system with additional Gas Chromatograph. The sampling valves for multicomponent system are controlled by FIRC-02. The pressure of the system is governed by pressure transducer-1 (PIRC-1) and dynamic valve-1 (DV-1) for pressure range at 20-150 bar. PIRC-2 and DV-2 are used to control the pressure for the range between 1 to 20 bar while PIRC-2 and vacuum pump are used to control the pressure below 1 bar. The adsorption isotherm is measured in the static mode. In this mode, gas is injected from FIRC-1 until the desired pressure is reached. Afterwards, all the valves are closed and the trapped gas is adsorbed until it reaches equilibrium.

The Magnetic Suspension Balance (MSB) is a very sensitive balance that is able to weigh samples contactlessly with a balance located at ambient conditions. The adsorbent

sample is located in the measuring cell and can be coupled or decoupled from the balance by a contactless magnetic suspension coupling. The principle of the MSB unit is illustrated in Figure A.3.

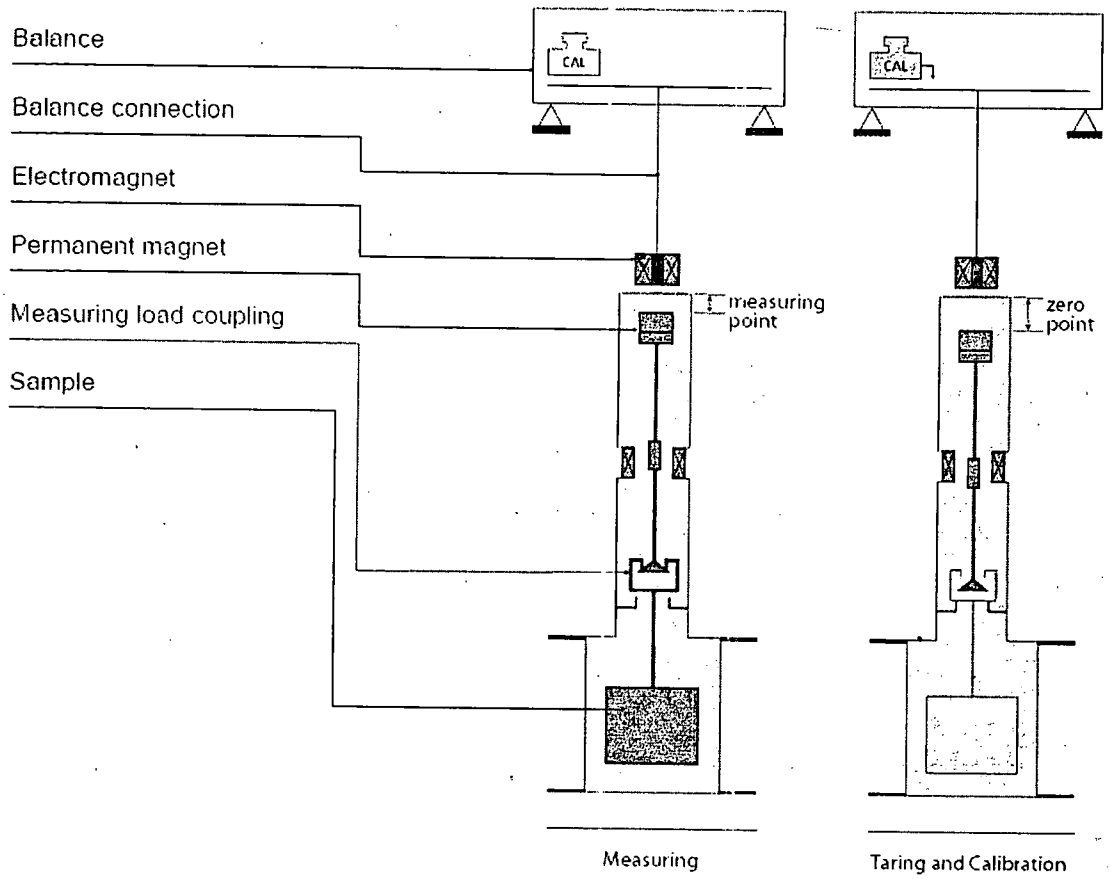


Figure A.3 Magnetic suspension balance unit.

The electromagnet, which is attached to the bottom of the magnetic balance, may control the suspension magnet to two different vertical positions. The suspension magnet consists of a permanent magnet, a sensor core and a measuring load decoupling cage. The first position is at the zero-point position (ZP) in which the suspension part suspends alone and does not contact to the load cage. This position represents an unloaded balance. The second position is measuring-point position (MP), in which the suspension part reaches a higher vertical position, thereby couples the sample to the balance and transmits the weight of the sample to the balance.

The density of the gas can be predicted through Equation of State (EOS) or measured simultaneously with the sorption measurement by using titanium sinker. This simultaneous measurement is needed if the buoyancy effect caused by the density of the

adsorptive fluid are large (high pressure and /or low temperatures) or for binary mixtures where EOS can lead to in accurate prediction. After the sorption measurement, the titanium sinker with known mass and volume is measured together with the adsorbent sample. From the MSB reading, the mass of the gas can be obtained thus the density also can be calculated. The simultaneous density measurement procedures is shown in Figure A.4 below.

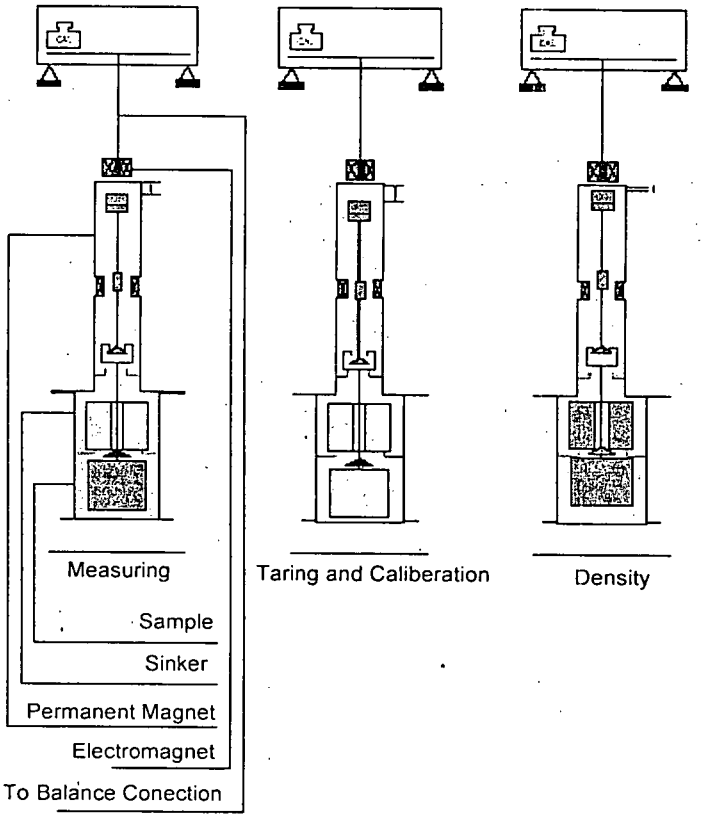


Figure A.4 Simultaneous density measurement procedures.

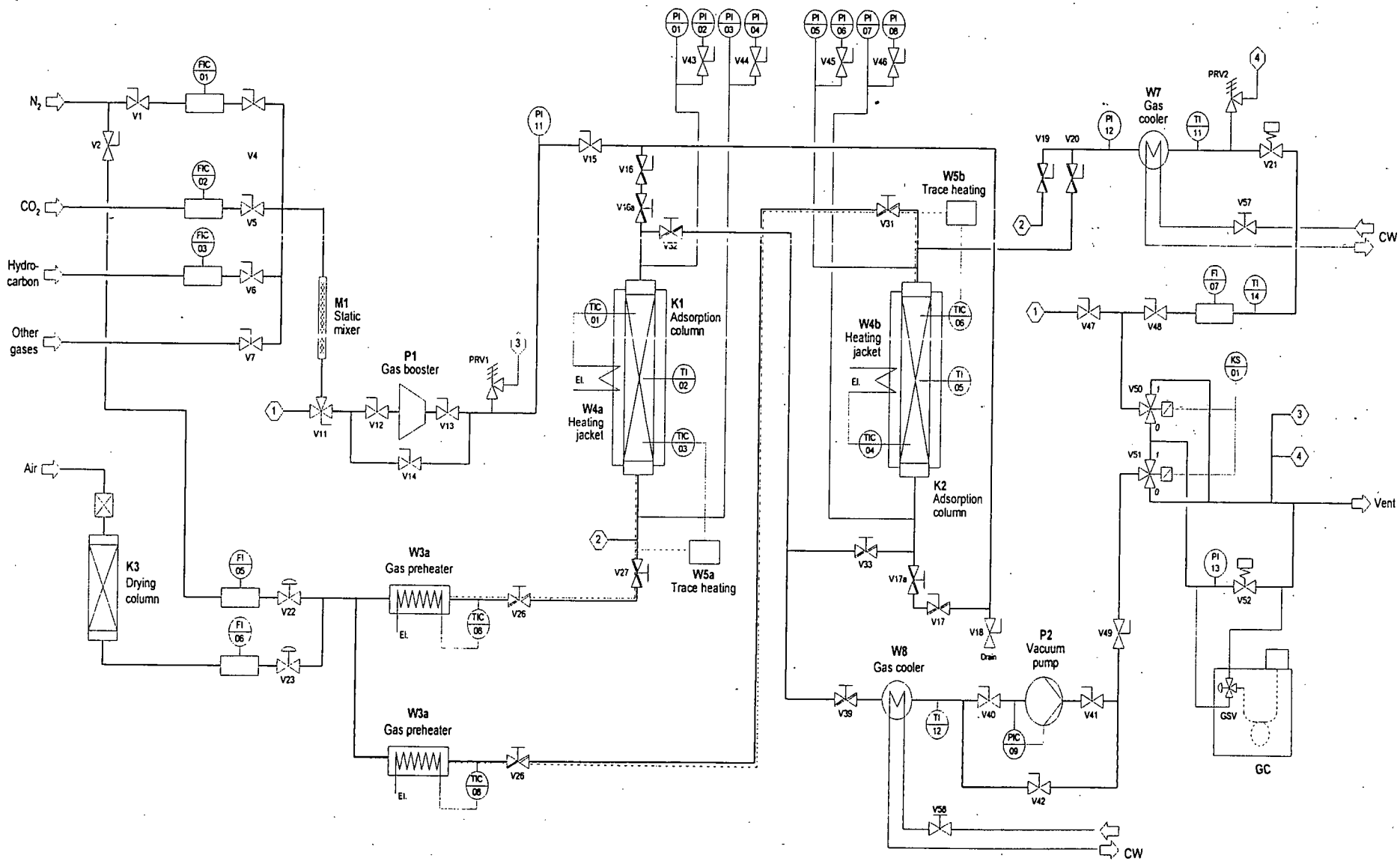
APPENDIX B
GAS ADSORPTION COLUMN UNIT

The schematic diagram of the experimental apparatus for dynamic studies is shown in Figure B.1. The Gas Adsorption Column Unit (GACU) consists of several equipments, instrumentations and control parts. These items are connected by 0.25 inch outside diameter (OD) Stainless Steel 316 tubings, Swagelok fittings and valves. The adsorption column is made from Stainless Steel (SS) 316 material with 1.5 inch internal diameter (ID) and 30 cm long.

Two types of adsorption column are available. The first type is the pressure column which designed for pressure up to 100 bar and temperature up to 200°C. The second type is the thermal column which is designed for pressures up to 20 bar temperatures up to 450°C. In this work, the second type was used for adsorption while the first type was used to build up the pressure. The length of the column can be adjusted by varying the position of the bed retainer at the support rod from 10 to 30 cm in height. The column is also equipped with three K-type thermocouples, which are positioned at three different heights (approximately 10 cm against each other).

Each column has a flow outlet point at the top for K1 and bottom for K2, which are all connected to a valve manifold. From the valve manifold, outlet gas is passed through gas cooler (W7) and exits through back pressure regulator (V21) to a sampling manifold. The back pressure regulator ensures that the system pressure is sustained while enabling the pressure to be adjusted at any value up to 100 bar. Other flow outlet points in the unit are located at the feed line through V47 and vent line through V49. All flow outlet lines are lead to the sampling manifold, which has two solenoid valves V50 & V51 to switch the flow of gas from the adsorption line or desorption line to either the GC for compositional analysis or out to vent. Sampling in the GC can then be carried out automatically via a gas sampling valve (GSV) at specific intervals set by the user.

Figure B.1 The schematic diagram of gas adsorption column unit (GACU)



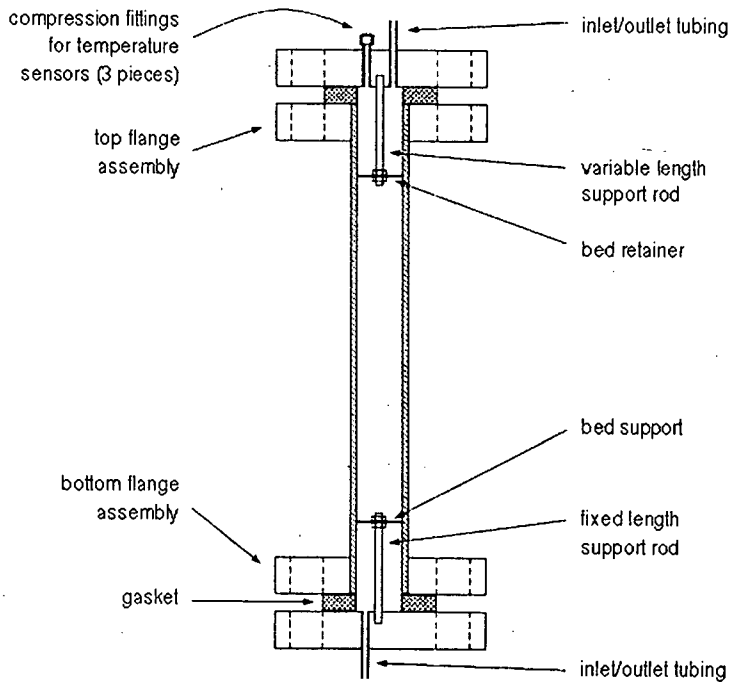


Figure B.2 Cross section of adsorption column.

The feed gases for the adsorption process were nitrogen, carbon dioxide, and methane supplied from gas cylinders. All the gas used has purity more than 99.99% and were supplied by MOX Bhd. Flow rate of each gas is controlled automatically using dedicated mass flow controllers. The different gas mixtures were thoroughly mixed in a static mixer (M1) before being fed to the column. The feed gas for adsorption can enter either column (K1) from the top or column (K2) from the bottom.

The flow rate of the gases is controlled by brooks Instrument model 5851i mass flow controller. The range of measurement is 0-5 NL/min and the accuracy of this controller is ±0.05 NL/min. The controller responses less than 6 second for 0 to 100% command step and the output signal used is 4-20 mA type.

For the desorption process, either nitrogen gas from the cylinder or compressed air can be used. In this research compressed air was used as the regenerant. Prior to the regeneration, the compressed air was pass trough a drying column (K3) filled with silica to remove moisture.. Both N_2 and air flow rates are regulated manually using needle valves (V22 and V23) and mass flow meters (FI 05 and FI 06). The gas preheater (W3) is

used to heat up the inlet gases to a set temperature before entering the column. Gas for desorption enters the column counter currently with feed gas for adsorption. An external heating jacket (W4) is provided for external heating of the column. Heat loss from the pipelines is compensated by using trace heating (W5) wrapped around the pipe surface. Outlet gas from the regeneration process flows through gas cooler (W8) and exit to the vent. Alternatively, Vacuum pump (P2) is also available at the vent line if the vacuum condition is required for the system.

The pressure of the adsorption column is measured at the gas inlet and outlet. The difference between these two pressure measurements is the pressure drop of the columns. However, in this study the pressure drop of the column was very small (< 0.1 bar) and can not detected accurately with the pressure transducer. The pressure is measured by Wika S10 Pressure transducer. In order to observe the pressure with higher accuracy, two pressure transducers with different range (high and low) were used. The working range of the low pressure transducer is at 0-10 barg pressure while the high pressure transducer working range is at 0-100 barg. Both pressure transducers have 0.25% of maximum scale accuracy and generate 4-20 mA type output signal.

The RIX micro boost compressor (P1) and the Swagelok 4R3A back pressure regulator valve (V22) control the pressure in the column. The gas is pressurized by RIX micro boost compressor (P1) while the pressure itself is controlled by the Swagelok 4R3A pressure regulator valve (V22). The compressor is able to increase the pressure of the mix gas up to 120 bar at 6 NL/min maximum capacity. The pressure of the system is controlled by adjusting the spring pressure of the back pressure regulator. The backpressure regulator is open when the system pressure is equal to the spring pressure. As the compressor continuously compress the gas, the pressure of the system increases and maintained at a constant pressure.

In order to reduce the pressure of the column at the regeneration step, ILMVAC vacuum pump MPC 201T was utilized. This vacuum pressure is able to generate ultimate vacuum pressure below 2 mbar. The maximum allowable inlet pressure and temperature of the vacuum pump are 1 bar and 60°C respectively. If the system pressure is higher than 1 bar, the pressure has to be reduced first by venting the stream by passing the vacuum

pump. For high temperature regeneration experiment, the inlet gas temperature should be cooled down by using gas cooler W8 before entering the vacuum pump.

The unit is equipped with pressure relief valves in order to prevent overpressure. The pressure relief valves can be adjusted to relieve the pressure based on the pressure requirement. In this research the pressure relieve valves is adjusted at 100 bar. However, this pressure value will not achieve since the maximum pressure used is only 20 bar.

The analysis of the adsorption outlet composition was carried out by Perkin Elmer Arnel-Clarus 500 gas chromatography equipped with Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID), installed in series. In this experiment, only the Thermal Conductivity Detector was used. Carboxen 1066 PLOT capillary column was used for the stationary phase in the GC while nitrogen was used as the carrier gas in the gas chromatograph. The carrier gas pressure and flow rate are 20 psi and 10 NL/min respectively. The GC oven temperature oven was 200 °C.

The purpose of analyzing the column outlet is to analyze the purity of the product and to determine when to stop the adsorption step. The adsorption step is terminated when the outlet composition is already equal with the inlet composition. The CO_2 content of the adsorption product is far smaller than the inlet composition. Therefore, different calibration curve will be used for different analysis purpose. The calibration was performed by injecting a known amount of mixtures directly to the GC.

VICI Valco instrument sampling valve is used to switch the gas sample to the gas chromatograph. The volume of the sample loop used is 1 ml which is relatively very small compare to the carrier gas amount ensure the sampling of the gas phase had a negligible effect. The sampling process is governed by programmable pneumatic controller which can be controlled from a PC by using Totalchrom Navigator Software. Purified air or nitrogen is used as the pneumatic fluid.

A POINTE CONTROLLER interface board for analog/digital conversion is connecting the equipment output signal and a Hawlet Packard DC 7100 CMT personal computer for data acquisition. The interface board is able to convert the analog signal to 12-bit digital data: SOLDAS data acquisition system is used to collect the 12-bit digital data and display in online or in historical pattern. TOTALCHROM Navigator version 6.3

software is used for raw gas chromatography data interpretation. The interpretation output is in the form of information of time retention and peak areas.

APPENDIX C

THE REPRODUCIBILITY OF EXPERIMENTAL DATA

C.1 Adsorption Isotherm Measurement

Table C.1 Reproducibility for adsorption isotherm measurements of CO_2 on 13X zeolite.

No	Pressure (bar)	Capacity 1 (mmol/gr)	Capacity 2 (mmol/gr)	Average Capacity Difference (%)
1	1.0	4.137	4.141	0.25
2	3.3	4.926	4.947	
3	5.2	5.142	5.170	
4	7.0	5.280	5.294	
5	9.0	5.383	5.366	
6	10.0	5.367	5.379	
7	20.4	5.612	5.632	
8	30.2	5.703	5.718	
9	40.2	5.729	5.747	
10	50.1	5.721	5.736	
11	60.1	5.697	5.715	

The average error for other experimental data is also within 0.25%.

C.2 Parametric Analysis

Table C.2 Reproducibility for dynamic study at 30% CO_2 concentration and flow rate of 5 NL/min.

No	Purity (%)	Recovery (%)	Purity Difference (%)	Recovery Difference (%)
1	99.89	90.56	0.005	2.64
2	99.89	88.23		

The average error for other experimental data in parametric analysis for both purity and recovery is below 5%.

APPENDIX D

CALIBRATION OF GAS CHROMATOGRAPHY

D.1 GC Calibration for High CO_2 Content

Table D.1 GC calibration data for high CO_2 content.

No	% CO_2	Area
1	25	202,746.96
2	33.3	249,374.02
3	50	330,822.83
4	40	284,241.61
5	60	369,225.22
6	80	454,903.83
7	90	491,865.43

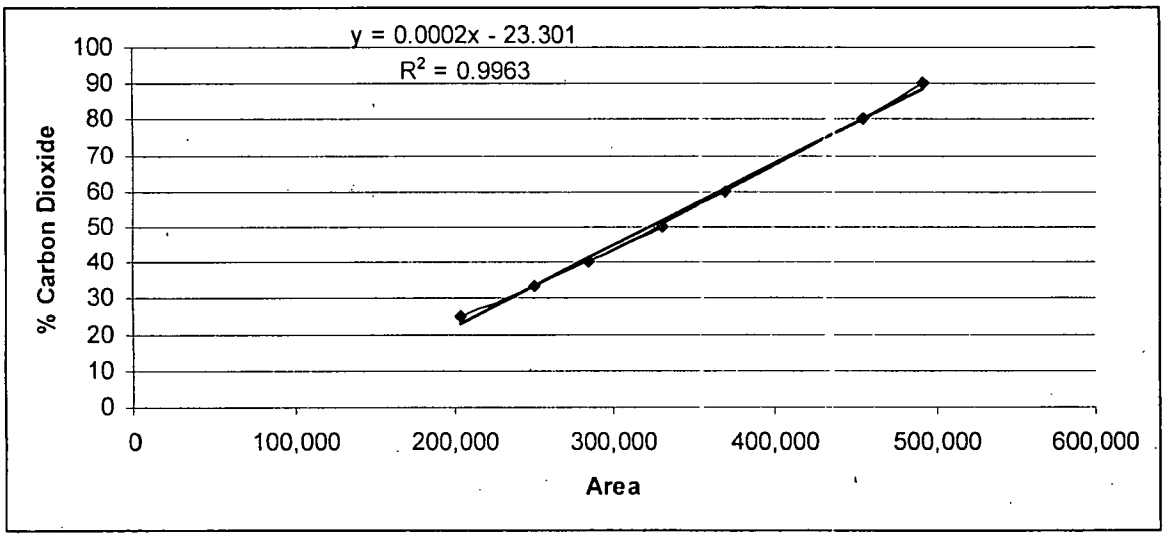


Figure D.1 GC Calibration curve for high CO_2 content.

The GC calibration equation for high percentage of CO_2 in outlet gas is given below:

$$\% CO_2 = 0.0002 \text{ (Area)} - 23.301 \qquad \text{(D.1)}$$

D.2 GC Calibration for Low CO_2 Content

Table D.2 GC calibration data for low CO_2 content.

No	% CO_2	Area
1	0.02	482.4567
2	1	16,036.63
3	3	49,396.25
4	5	75,828.73
5	7	106,189.5

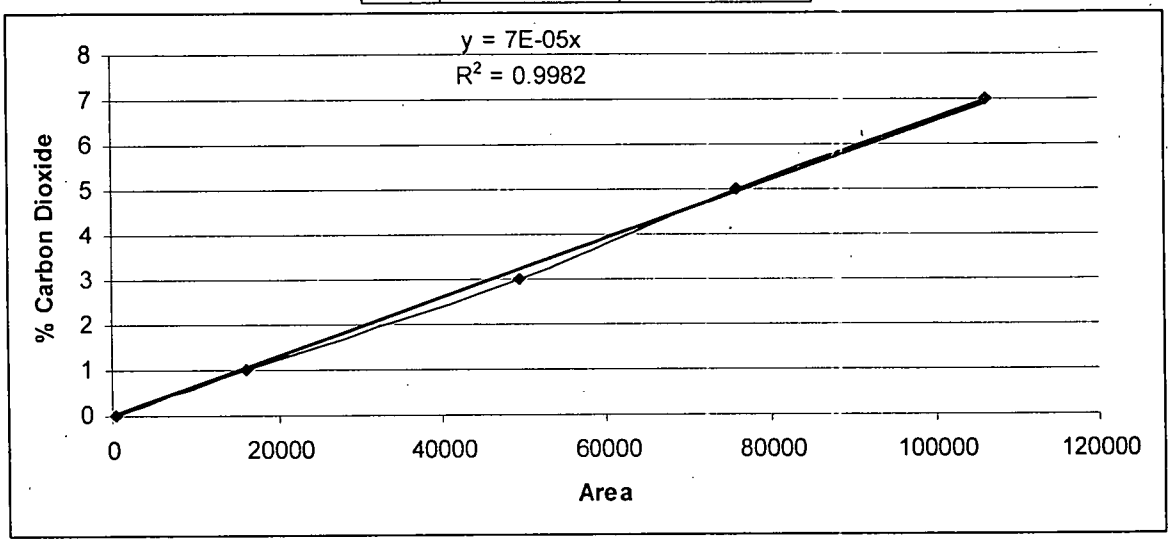


Figure D.2 GC Caliberation curve for low CO_2 content..

The GC calibration equation for low CO_2 concentration in product is given below:

$$\% CO_2 = 7x10^{-5}(\text{Area}) \qquad (D.2)$$